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THE GEOLOGY OF URANIUM

TODAY, WORLDWIDE INTEREST in fissionable material has focused more attention than ever on uranium—*the origin of its deposits, its mineralogy, and methods of investigation.* As a result, the Soviet *Journal of Atomic Energy* devoted an entire supplement (No. 6) to current problems on the geology of uranium, which was published December, 1957 in Russian.

Now this collection of twelve important papers by leading Soviet specialists is available, in English, for those Western scientists who must keep abreast of the latest developments in the field by their Russian counterparts. Here, in well written and concise style, are graphic expositions of the main problems encountered in current investigations, with attention directed mainly toward *the study of uranium deposits which formed contemporaneously with sedimentary rocks.* The important role of *diagenesis* and of subsequent *epigenetic and metamorphic* phenomena, which have produced redistribution and concentration of uranium under favorable geological conditions, is clearly illustrated by actual occurrences; processes which lead to formation of epigenetic infiltration uranium deposits in coal basins are keenly analyzed; and various hypotheses, reported in Soviet and foreign literature, on the origin of such deposits are discussed in detail.

Additionally, this new work covers *a comprehensive survey of aerial geophysical methods* in various countries; *methods for radiometric study of uranium in three-component ore containing radioactive elements of the uranium and thorium series;* a description of several *new* minerals (including recent data on *nenadkevite,* described earlier in the journal *Atomic Energy*); and the results of *thermal investigations* conducted on a number of uranium minerals, which, on the whole, open the door to the possibility of determining other minerals difficult to analyze. In short, this richly-authoritative volume not only reveals the most up-to-date Soviet progress, but also adds *new* knowledge to our growing storehouse of information and stimulates incentive for further investigation into THE GEOLOGY OF URANIUM.

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
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1958, No. 8 August

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CORROSION OF SILICATE GLASSES BY ALKALINE SOLUTIONS

COMMUNICATION 4. CORROSION OF GLASSES BY SOLUTIONS OF VARIOUS HYDROXIDES

V. S. Molchanov and N. E. Prikhid'ko

The peculiarity of the action of alkaline solutions on silicate materials, which distinguishes these reagents from solutions of acids and salts, lies in the breakdown of silica and polymeric silicon-oxygen radicals by hydroxyl ions into simple groups and, in the limit, into orthosilicate ions SiO_4^{4-}. It is natural to suppose that the action of an alkaline solution on glass will vary symbatically with the chemical activity of the solution, which is associated, in its turn, with the electrolytic dissociation of the hydroxide. It might be thought, therefore, that solutions of hydroxides of a given type in equivalent concentrations at the same temperature could be placed in the following series with respect to the intensity of their action on glasses: KOH > NaOH > LiOH and $Ba(OH)_2$ > $Sr(OH)_2$ > > $Ca(OH)_2$ in accordance with the dissociation constants of the hydroxides, as given in Table 1.

TABLE 1
Average Values of Dissociation Constants at 25° According to Gimblett and Monk [1]

Hydroxide	Dissociation	Hydroxide	Dissociation
LiOH	0,5—1,2	$CaOH^+$	0,043
NaOH	3,7—5,9	$SrOH^+$	0,150
KOH	8% higher than that of NaOH	$BaOH^+$	0,230

Despite the conventional nature of the concept of "dissociation constant" in its application to strong electrolytes, these values, deduced from the electrochemical properties of the corresponding solutions, characterize qualitatively the chemical activities of various hydroxides in reactions proceeding with the participation of hydroxyl ions. In particular, the order in which potassium and sodium hydroxides is placed above is required by their activity coefficients in 0.5 N solutions [2], their electroconductivities (according to Arrhenius's data [3]), and their conventional pH values (according to Schwarzenbach and Sulzberg [4]).

However, when we examine the literature on the stability of glasses to various alkalis, we find that almost all investigations suggest that there are systematic departures from these series of hydroxides. Thus, in a comparison of the actions of solutions of alkaline-earth hydroxides on silica gel and laboratory glass, Jones [5] found that calcium hydroxide was the most active. The effects of a greater variety of hydroxides were determined by Hubbard and Rynders [6], who found that alkalis can be placed in the following order with respect to their corrosive effects on McInnes electrode glass: NaOH > LiOH > KOH > $Ba(OH)_2$ > NH_4OH.

Whereas the position assigned by Hubbard and Rynders to lithium hydroxide in this series may give rise to some doubt, the relative positions of sodium and potassium hydroxides are confirmed by all published investigations on this question.

EXPERIMENTAL

In a study of the effect of the composition of glass on its stability to the action of alkalis we observed that sodium hydroxide has the greatest corrosive effect on glasses of the type 13% $Na_2O \cdot (87 - X)\%$ $SiO_2 \cdot X\%$ RO, in which R is beryllium, magnesium, calcium, zinc, or cadmium (experimental glasses; the composition is given in moles percent), and on commercial optical flint glasses. By way of examples, in Tables 2 and 3 we give the thicknesses (μ) of the layers of glass dissolved, as measured interferometrically [7]. Glasses were subjected to the

action of 0.5 N solutions of sodium, potassium, and ammonium hydroxides for four hours at 90°. As ammonia solutions are thermally unstable, we first established the way in which their concentrations fell for the same evaporation area (about 85 cm^2), volume of solution (950 ml), and time is applied during the actual measurements (concentrations were determined by titration). As will be seen from the figure, when we start with 0.8 N ammonia, the solution remaining after four hours has a strength of 0.3 N. Taking account of the very small effect of alkali concentration (for values ranging up from 0.25 N) on the corrosion of complex glasses [8], we may assume without appreciable error that the action of this solution of ammonia is equivalent to that of a stable 0.5 N solution. As will be seen from Tables 2 and 3, ammonium hydroxide, in keeping with its weakly alkaline character, corrodes glass much less than the strong alkalis sodium and potassium hydroxides. Moreover, there is a constant difference between the effects of sodium and potassium hydroxides, and this is in a direction opposite to that generally accepted for these substances: sodium hydroxide attacks glass to an appreciably greater extent than potassium hydroxide.

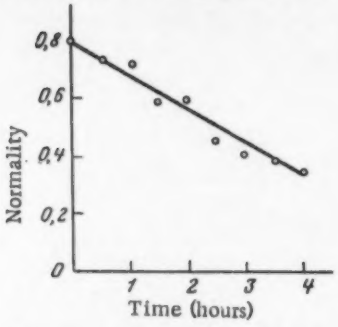

Fig. Variation with time of the concentration of NH_4OH at 90°.

It is worth noting that a comparison of the corrosions of glasses in sodium and potassium carbonate solutions of equivalent concentrations [9-11] shows that sodium carbonate is always the more powerful agent. Hence, the higher tendency for silicate glasses to be corroded by solutions of sodium compounds must be regarded as established beyond doubt. For this phenomenon we propose the term "sodium anomaly," and we shall use this term in what follows.

TABLE 2

Thicknesses (μ) of Layers of Glass Dissolved in 0.5 N Solutions of Various Hydroxides

No.	Glasses of the type: 13%Na_2O·(87−X)%SiO_2·X%RO					No.	Glasses of the type: 13%Na_2O·(87−X)%SiO_2·X%RO				
	bivalent metal R	X (mole %)	reagent				bivalent metal R	X (mole %)	reagent		
			NaOH	KOH	NH_4OH				NaOH	KOH	NH_4OH
1	Beryllium	12	0,9	0,6	0,1	11	Zinc	5	1,5	1,1	0,1
2	"	22	0,8	0,7	0,2	12	"	12	2,0	0,8	0,2
						13	"	17	2,4	1,0	0,3
						14	"	22	2,7	1,3	0,4
3	Magnesium	12	1,4	0,9	0,3	15	"	27	2,9	1,8	0,6
4	"	17	1,5	1,2	0,4	16	"	32	3,5	2,8	0,8
5	"	32	1,9	0,9	0,5						
						17	Cadmium	5	1,0	0,7	0,3
6	Calcium	5	1,3	0,9	0,4	18	"	12	1,3	0,5	0,1
7	"	12	0,9	0,5	0,5	19	"	17	1,3	0,7	0,2
8	"	17	1,0	0,7	0,6	20	"	22	1,3	0,8	0,3
9	"	22	1,0	0,9	0,7	21	"	27	1,4	1,0	0,5
10	"	27	1,4	1,1	1,0	22	"	32	1,5	1,0	0,8

The sodium anomaly has not yet been explained. As working hypotheses requiring experimental verification we may have the following: 1) in spite of accepted views, sodium hydroxide is a stronger alkali than potassium hydroxide; 2) the formation of sodium silicates proceeds more readily with a greater gain of energy than the formation of the silicates of other metals, so that sodium hydroxide corrodes silicate glasses more strongly than the other hydroxides; 3) for the breakdown of silicate glasses by alkaline solutions not only the interaction of hydroxyl ions with silicon-oxygen groups is of significance, but also ion exchange, i.e., the exchange of cations of metals entering into the composition of the glass for cations of the alkali in the solution. The exchange of ions weakens the structure of the glass and makes the silica skeleton prone to the action of hydroxyl ions. If we assume further that sodium ions are more capable of undergoing exchange than other ions, we have the possible cause of the sodium anomaly.

The first hypothesis is contrary to the behavior of alkalis in all reactions except the corrosion of silicate glasses, and it therefore seems the least probable. Choice between the remaining explanations may be helped

by a comparison of the effects of hydroxides on glasses containing cations having different tendencies to undergo exchange. We therefore studied the corrosion of eight silicate glasses belonging to quite different families (Table 4). Glass 1 was a quartz glass for which ion exchange could not play any part. Glasses 6 and 8 were multicomponent glasses which did not contain alkali metals, the cations of which are the most mobile and most prone to exchange. Glasses 2-5 and 7 contained different alkali metals or differed in other components, and with these glasses ion-exchange processes should proceed with different degrees of readiness.

TABLE 3
Thicknesses (μ) of Layers of Glass Dissolved in 0.5 N Solutions of Various Hydroxides (Industrial Glasses and Optical Flint Glasses)

No.	Type of glass	Reagent		
		NaOH	KOH	NH_4OH
1	F1	2,3	1,6	0,6
2	F3	2,2	1,6	0,6
3	F4	3,1	1,4	0,6
4	TF 1	3,0	1,6	0,6
5	TF 2	3,5	1,8	0,6
6	TF 3	3,5	2,6	0,9
7	TF 5	5,1	1,6	1,4
8	TF 7	5,7	3,2	1,7
9	TF 10	6,4	3,7	1,3

For all the glasses we determined the thickness of the layer dissolved under the conditions and by the procedure indicated above. The reagents acting on the glasses were 0.5 N solutions of lithium, sodium, and potassium hydroxides and 0.02 N solutions of calcium, strontium, and barium hydroxides. In view of the fact that alkaline-earth hydroxides should have a much feebler action than alkali-metal hydroxides, it was decided to check also the action of water on the glasses under the same conditions as those used in the measurements of alkali-stability (90°, 4 hours). The possibility was not excluded that water would not only leach the glasses, but also dissolve them as a whole, for it was known from Dubrovo and Shmidt's experiments [12] that the leaching of sodium silicates, which occurs at 40°, is replaced by complete dissolution at higher temperatures. This is associated mainly with secondary reactions between the glass and the alkaline extract of its components formed in the initial period of the interaction between the glass and water. When we are dealing with the greater thicknesses of the layers of glass dissolved under the action of strong hydroxide alkalis, such "autopeptization" of glass can be neglected. With weak alkalis, however, it is possible that this phenomenon should be taken into account. The results of the corrosion measurements on glasses are given in Table 4.

TABLE 4
Thicknesses (μ) of Layers of Glass Dissolved in Hydroxide Solutions

No.	Characteristics and composition (mole %) of glass	0.5 N solutions			0.02 N solutions			H_2O
		LiOH	NaOH	KOH	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$	
1	Quartz glass	0,3	0,8	0,6	0,05	0,2	0,4	<0,01
2	Optical 50,8 $PbO \cdot 0,6K_2O \cdot 48,6\ SiO_2$	3,8	25,3	4,8	0,6	3,8	2,0	0,4
3	Experimental $17Na_2O \cdot 13PbO \cdot 70SiO_2$	1,4	2,8	2,2	0,05	1,1	1,7	0,5
4	Experimental $17K_2O \cdot 13PbO \cdot 70SiO_2$	1,8	2,5	2,3	0,2	1,7	2,6	0,2
5	Experimental $13Na_2O \cdot 32BaO \cdot 55SiO_2$	2,3	4,9	4,0	0,05	3,0	3,0	0,03
6	Optical alkali-free barium borosilicate glass TK10	4,8	7,1	6,9	0,2	3,0	2,2	0,3
7	Experimental $7Na_2O \cdot 23B_2O_3 \cdot 70SiO_2$	11,6	104,0	24,0	3,3	18,7	8,3	3,0
8	Optical alkali-free antimony borosilicate glass O2	3,4	17,2	7,5	1,1	2,8	3,9	5,0

It will be seen from Table 4 that, with the exception of sodium hydroxide, and of strontium hydroxide when acting on Glasses 2 and 6 the remaining hydroxides form a sequence with respect to their corrosive action on silicate glasses which follows their dissociation constants and is the same as that observed for other reactions: $KOH > LiOH > Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2$.

The operation of this rule is seen particularly clearly in the case of vitreous quartz, the reaction of which with alkalis is not complicated by secondary reactions of the glass with the products of its own breakdown. In the above series we may place aqueous ammonia between lithium and barium hydroxides because, according to the data of Table 2, in the effectiveness of its action on vitreous silicates it is less than half as strong as potassium hydroxide (in this sense, lithium hydroxide was found to be weaker than potassium hydroxide by a factor of 1.5 to 2 in all cases investigated by us). At the top of the series of hydroxides we must place sodium hydroxide, which has a stronger action on all glasses than any other hydroxide. This again confirms that the sodium anomaly applies to glasses of all compositions. Difficulties in observing it will probably arise only in the study of very unstable glasses, which are corroded to an extent commensurate with the sensitivity of the method of measurement.

The corrosion of glasses by solutions of hydroxides of the alkaline-earth hydroxides proceeds in a very peculiar way. Here, in addition to the corrosive effect of hydroxyl ions there is interaction between the cation of the hydroxide and the active silica of the glass, which results in inhibition of further corrosion. The deposition of layers of $Ca(OH)_2$ crystals cannot be excluded; this is discussed by Sasaki [13], who showed that in the treatment of quartz glass with $Ba(OH)_2$ or $Sr(OH)_2$ the corresponding silicates are formed, but $Ca(OH)_2$ crystals are deposited in a $Ca(OH)_2$ solution. The inhibition of the effect is particularly marked in the case of calcium ions. Thus, $Ca(OH)_2$ solution had a more feeble corrosive effect on Glasses No. 3, 4, 6, and 8 than an extract of their own breakdown products did. These facts, incidently, compel us to regard the above-mentioned conclusions of Jones [5] as incorrect. The solutions of all the other hydroxides, particularly the alkali-metal hydroxides, have a much stronger action than water. It must be emphasized that water at 90° dissolves layers of readily measurable thickness from all glasses except quartz. It is evident, however, that true leaching does occur at lower temperatures.

It is difficult to explain the results obtained for the action of strontium hydroxide on Glasses No. 2, 5, 6, and particularly 7; strontium hydroxide here shows a phenomenon similar to the sodium anomaly. Though we may still attempt to interpret such behavior in Glasses No. 5 and 6 as the result not of more intense action of strontium hydroxide, but of less intense action of barium hydroxide on glasses rich in barium (to which the formation of barium silicates on the surface contributes), in the case of Glass No. 7 the greater corrosive power of strontium hydroxide is so notable that it cannot be regarded as apparent. The explanation of these peculiarities requires still further investigation. We consider, however, that since the more intense effect of strontium hydroxide is not associated with the universality that is so characteristic of the sodium anomaly, these two phenomena have different causes.

Let us return now to the explanation of the sodium anomaly. In considerations relating to its mechanism an important fact to take into account is the greater corrosion produced by sodium hydroxide in all glasses, including alkali-free glasses and particularly quartz glass. This indicates that cation-exchange processes do not play a determining role in this phenomenon. This eliminates the third of the possible explanations of the sodium anomaly enumerated above, and only the second remains: the presence of sodium ions facilitates the breakdown of the silicon-oxygen groups of the glass and their peptization by hydroxyl ions with formation of ions of silicon oxy-acids. This view, of course, may be regarded rather as a description of the phenomenon than as an explanation. However, the data available to us at present do not permit us to give a more exact explanation. As the sodium anomaly is of interest not only to silicate chemists, but also to workers on the problem of the chemical activity of bases, we may expect that it will be studied more extensively and will be completely explained in the course of time.

SUMMARY

1. The hydroxides examined in the present investigation may be arranged in the following order with respect to corrosive action on glasses: $KOH > LiOH > NH_4OH > Ba(OH)_2 > Sr(OH)_2 > Ca(OH)_2$.

2. Sodium hydroxide corrodes silicate glasses of all compositions to a greater extent than all the other hydroxides. It is proposed to call this phenomenon the "sodium anomaly." The sodium anomaly probably arises from peculiarities in the peptization of silicon acids by hydroxyl ions in presence of sodium ions.

3. The action of hot water (90°) on silicate glasses of low stability consists not only in leaching, but also to a considerable extent in dissolution. The thickness of the layer of glass dissolved is sometimes commensurate with that dissolved by the hydroxides.

4. As the result of the formation of alkali-stable calcium silicates on the surface of the glass, the corrosive effect of solutions of calcium hydroxide is generally less than that of water.

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RELATION OF THE ACTIVITIES AND STABILITIES OF NICKEL–ALUMINA CATALYSTS TO THE MACROSTRUCTURE OF THE CARRIER

L. Kh. Freidlin, A. A. Balandin, N. V. Borunova, and A. E. Agronomov

Three particularly important functions of a catalyst carrier can be regarded as firmly established. The carrier preserves the catalysts from recrystallization, increases the active surface of the catalyst, and increases its selectivity. Study of the effect of the character of the macrostructure of the carrier therefore acquires great importance. As the most uniform distribution of nickelous oxide on alumina is attained by coprecipitation, investigators have very frequently used nickel-alumina catalysts prepared in this way in their work.

The effect of macrostructure on the activity of nickel-alumina catalysts of various nickel contents prepared by the coprecipitation method was studied by Agronomov and Mardashev [1]. We now describe an investigation on the relation between the macrostructure of the alumina and the activities and stabilities of nickel-alumina catalysts prepared by the deposition method. It might be thought that for the maximum increase in the active surface of the catalyst it would be necessary to use alumina with as great a specific surface as possible. However, such carriers usually have small pore radius, and the pores may be inaccessible both to the nickelous oxide applied and to the reactants. On the other hand, if a coarsely porous alumina were used, its specific surface might be too small and its activity would probably be low. There arises the question, therefore, of the optimum macrostructure of alumina.

The study of this question is all the more important in that references have been made in various papers to the low activity of nickel catalysts prepared by the deposition method. Thus, Shuikin and co-workers [2] states that the activities of catalysis prepared by the deposition of nickel (2-4%) on birch charcoal are low for the dehydrogenation of cyclohexane: conversions of 30-40% are obtained. The stabilities of such catalysts are low: after 2000 minutes their activities are reduced by factors of 3-4. However, these catalysts are highly active and stable for the hydrogenation of aromatic hydrocarbons. Novikov and co-workers [3] found that nickel catalysts prepared by the decomposition of the formate on active charcoal are highly active and stable for the hydrogenation of alkenes, cycloalkenes, and aromatic hydrocarbons. Catalysts prepared by the application of nickel formate to alumina also showed low dehydrogenating activity. In the present investigation we studied the activities of four nickel catalysts prepared by the deposition of nickel on alumina samples differing in macrostructure.

EXPERIMENTAL

1. Nickel-alumina catalysts were prepared from the following four samples of alumina: Alumina 1, prepared by precipitation of aluminum nitrate with ammonia at 20°; Alumina 2, prepared by the decomposition of aluminum nitrate at 500°; Alumina 3, prepared from aluminum hydroxide by the reprecipitation method (in stalk-shaped pieces); Alumina 4, which was commercial alumina. All the alumina samples were roasted at 500° for four hours. The alumina was impregnated with 0.5 M nickel nitrate, which was evaporated with constant stirring, and the mass was formed into 6 × 4 mm grains, which were roasted at 400° until oxides of nitrogen ceased to be evolved (4 hours). After the decomposition, the composition of the mixture of oxides corresponded to 12.5% of nickelous oxide and 87.5% of aluminum oxide. Reduction was carried out with electrolytic hydrogen at 350° for ten hours. The activity of the catalyst was characterized by the extent of dehydrogenation of cyclohexane, as determined refractometrically [4]. The dehydrogenation reaction was carried out discontinuously (8 hours per day) at 300° at a space velocity of 0.3 hour^{-1}. The composition of the gas liberated was determined in a VTI apparatus.

The specific surface was measured in a high-vacuum apparatus containing a McBain quartz spring balance [5]. Adsorption isotherms for benzene vapor at 0° were determined. Specific surfaces were calculated by the BET method [6] on the assumption that the benzene molecule occupies an area of 46.5 A^2 [7]. The characterization of the macrostructures of the alumina samples and the catalysts prepared from them* is given in the Table and in Figs. 1 and 2.

TABLE

No.	Samples investigated	Specific surface (m^2/g)	Total amt. of adsorbed benzene (m moles/g)	Max. of pore vol. distribution with respect to radius (A)	Range of pore dimensions (A)	Extent of dehydrog. of cyclohexane (%)
1	Al_2O_3 prepared by precip. with NH_3	440	3,20	13	10—18	—
	Ni — Al_2O_3	410	2,70	—	—	49,0
2	Al_2O_3 prepared by decomp. of the nitrate	110	1,08	—	10—15	—
	Ni — Al_2O_3	160	1,46	—	10—15	60,0
3	Al_2O_3 prepared by reprecipitation	280	5,00	40	20—120	—
	Ni — Al_2O_3	360	4,42	30	20—120	92,0
4	Commercial Al_2O_3	160	3,62	50 (diffuse)	20—120	—
	Ni — Al_2O_3	170	3,30	50 (diffuse)	20—120	83,2

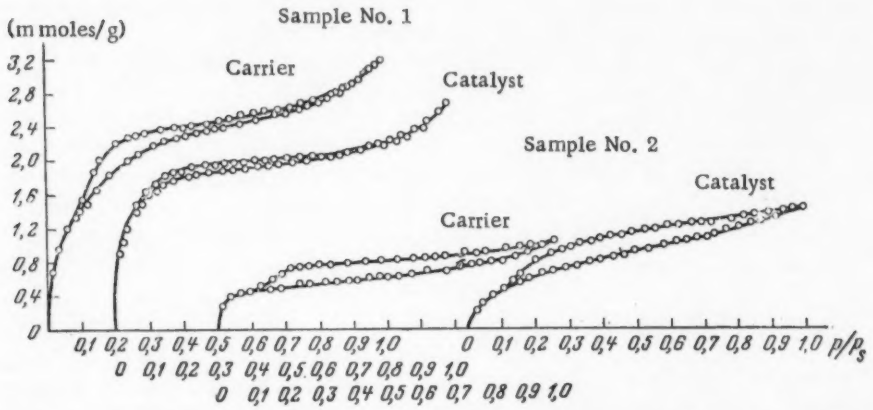

Fig. 1. Sorption isotherms for benzene vapor on Aluminas No. 1 and 2 and on nickel-alumina catalysts prepared from them: Alumina 1, prepared by precipitation with ammonia; Alumina 2, prepared by decomposition of the nitrate.

2. It follows from the Table and Fig. 1 that Alumina 1, prepared by precipitation of the nitrate from solution with ammonia, has the highest specific surface, 440 m^2/g, but has very fine pores, 10-18 A (13 A at the maximum of the pore volume distribution with respect to radius). When nickel is deposited on the sample of alumina, the

* The macrostructures of the reduced catalysts were investigated.

pores are covered with nickel and their inner surface becomes inaccessible to reactant molecules; this results also in some reduction in specific surface after the deposition of nickel. In spite of the great specific surface, this catalyst has the lowest catalytic activity: the extent of dehydrogenation of cyclohexane is 49%. Catalyst 2 is also of low activity; it has fine pores, radii 10-15 A (see Table and Fig. 1).

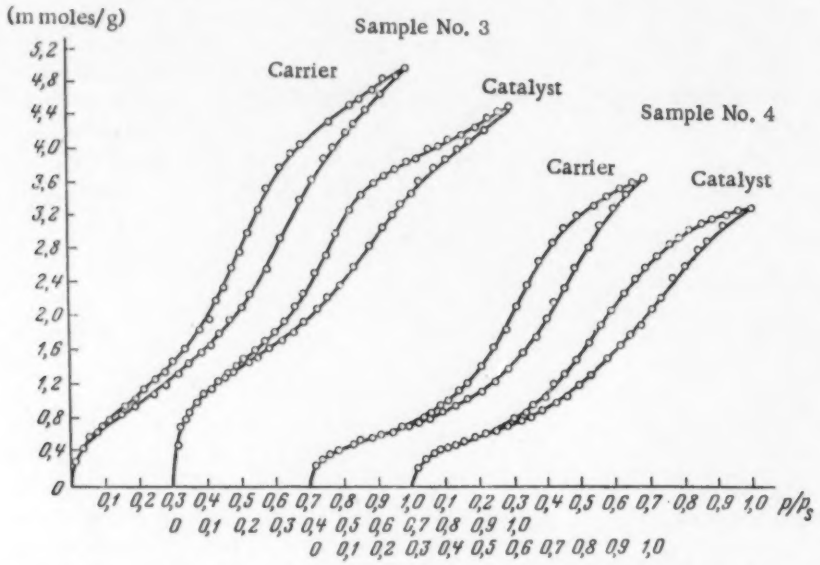

Fig. 2. Sorption isotherms for benzene vapor on Aluminas No. 3 and 4 and on nickel-alumina catalysts prepared from them: Alumina 3, prepared by reprecipitation; Alumina 4, commercial.

Alumina 3 has a specific surface of 280 m^2/g. The maximum on the curve for pore volume distribution with respect to radius is 40 A. As will be seen from the table and Fig. 2, Alumina 3 is not homogeneously porous. After deposition of nickel on this alumina the specific surface rises from 280 to 360 m^2/g. It appears that the nickel, in reproducing in the main the relief of the carrier surface, has a microroughness of structure, so that some increase in specific surface occurs. At the same time the maximum of the pore volume distribution with respect to radius moves to a smaller radius, probably as a result of the covering of the internal surface of the pores with nickel. This catalyst has the highest activity: the extent of dehydrogenation of cyclohexane attains 92%. The specific surface of Alumina 4 is much smaller, but the maximum of the pore volume distribution with respect to radius is at a somewhat greater radius than for Alumina 3. The table shows that, even with its considerably smaller specific surface, this catalyst has high catalytic activity: the extent of dehydrogenation of cyclohexane is 83.0%.

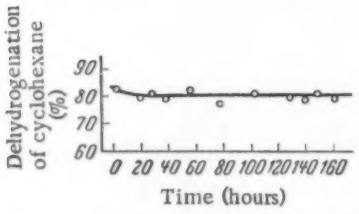

Fig. 3. Stability of nickel-alumina Catalyst 4 in the dehydrogenation of cyclohexane.

Comparison of the results obtained with Catalysts 1 and 2, prepared by the deposition of nickel on finely porous samples of alumina, shows that they are both of low activity, though the specific surface of the carrier of one of them is four times as great as that of the carrier of the other: 440 and 110 m^2/g, respectively. Comparison of the results obtained with catalysts 3 and 4, prepared by the deposition of nickel on coarsely porous samples of alumina, shows that they have high activity in the dehydrogenation of cyclohexane. The difference in their activities is comparatively small, though the specific surface of the carrier of one of them is almost double that of the other (280 and 160 m^2/g, respectively).

Hence, the activities of nickel-alumina catalysts prepared by the deposition method are determined mainly not by the specific surface, but by the character of the porosity of the alumina on which the nickel is deposited.

3. The most important cause of the deactivation of nickel-alumina catalysts in the dehydrogenation reaction is the blocking of the active surface by a carbonaceous layer. The effect of the carbonaceous film is particularly notable in finely porous catalysts because of the difficulty in the removal of reacting components from them. It is natural to suppose that the stability of the catalyst is also associated with the character of the porosity of the carrier. It was shown previously that the vapor-phase hydrolysis of chlorobenzene on finely porous silica gel is complicated by side reactions and that the catalyst is of low stability [8]. When the silica gel is promoted with copper, the hydrolysis reaction is transferred from the fine pores to the coarser ones in which the copper appears to be adsorbed [9]; side reactions are therefore absent, and the catalyst is stable. By analogy it may be supposed that in the case of nickel-alumina catalysts prepared by the deposition method, dehydrogenation proceeds mainly in the coarser pores. It may therefore be expected that in such catalysts the pores will be carbonized very slowly.

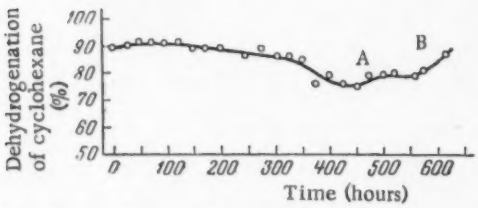

Fig. 4. Stability (in the dehydrogenation of cyclohexane) of a nickel-alumina catalyst prepared by the deposition of nickel on Alumina 3 after treatment with steam under pressure: A) first regeneration; B) second regeneration.

In the present investigation we studied the stabilities of two catalysts prepared by deposition on coarsely porous samples of alumina. Figure 3 shows the time-dependence of the extent of dehydrogenation of cyclohexane on a nickel-alumina catalyst in which the carrier was Alumina 4. It will be seen that the activity of the catalyst is preserved almost unchanged over a period of 160 hours. As we showed previously, treatment of alumina with steam under pressure results in a sharp fall in its specific surface, but the pores are widened greatly [10]. In the present work we made use of the coarsely porous carrier prepared in this way. The sample used had the following structural characteristics: specific surface 240 m^2/g, predominant radius of transitional pores 45 A. As was expected, the catalyst prepared by the deposition of 10% of nickel on this alumina was highly active in the dehydrogenation of cyclohexane: extent of dehydrogenation 89.2%. We investigated its stability in the dehydrogenation reaction under the conditions described above. The results are represented in Fig. 4. Figure 4 shows that in the first 200 hours the extent of dehydrogenation of cyclohexane is 89-91%. After 330 hours the activity is somewhat lower (85%), and after 450 hours the activity is 75.0%. The catalyst was regenerated by oxidation in a stream of air at 400° for four hours and subsequent reduction at 350° for 12 hours. As will be seen from Fig. 4, the activity of the catalyst rose, and the extent of dehydrogenation of cyclohexane increased to 80.0%. Its activity then stayed at this level for 100 hours. Regeneration was repeated with more prolonged oxidation (10 hours) and reduction (15 hours). After the second regeneration the activity of the catalyst was almost completely restored: the extent of dehydrogenation of cyclohexane was 87.0%. In the course of the work the liberated gas was analyzed on several occasions. It was found that it consisted of pure hydrogen, i.e., the reaction does indeed proceed without degradation of the ring.

These results show that catalysts prepared by the deposition of nickel on coarsely porous samples of alumina have considerable stability in the dehydrogenation of cyclohexane.

SUMMARY

1. The relation of the activities and stabilities of nickel-alumina catalysts to the character of the macrostructure of the alumina was studied.

2. A particularly high specific surface is not necessary for a carrier of a highly active nickel-alumina catalyst; its dehydrogenating activity is determined mainly by the character of the porosity of the carrier.

3. Catalysts prepared by the deposition of nickel on coarsely porous alumina have high activities and stabilities, but those having a finely porous alumina as carrier have considerably lower activities.

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PROPERTIES AND STRUCTURE OF NiO–Al_2O_3 CATALYSTS

COMMUNICATION 2. X-RAY STUDY OF THE EFFECT OF THE PROPORTIONS OF COMPONENTS AND THE CONDITIONS OF THERMAL TREATMENT ON PHASE COMPOSITION AND CRYSTAL STRUCTURE

A. M. Rubinshtein, V. M. Akimov, and L. D. Kretalova

Investigation [1] of the activity and selectivity of NiO–Al_2O_3 catalysts prepared by coprecipitation at a final pH of 8 for the decomposition of i-C_3H_7OH provided chemical proof of interaction between the components in solid NiO–Al_2O_3 catalysts and gave some indication of their phase composition. These conclusions were in need of direct verification by physical methods, particularly x-ray structure analysis. A detailed x-ray investigation of NiO–Al_2O_3 catalysts appeared to be all the more desirable in that our first structural measurements revealed very serious discrepancies with the results and conclusions obtained for this binary system of Milligan and Merten [2].

These authors studied gels of nickel and aluminum hydroxides prepared by coprecipitation under various conditions; these were air-dried and roasted at 500°, 700°, and 1000°, and x-ray examination then showed that above 700° samples containing equimolecular amounts of NiO and Al_2O_3 form the spinel $NiAl_2O_4$, which forms solid solutions with both NiO and Al_2O_3. At lower temperatures the mutual protective action of the gels and oxides was so strong that over a wide range of concentrations (e.g. 20-50 moles % Al_2O_3 at 500°) the samples had an amorphous structure; at a lower Al_2O_3 content only the diffraction pattern of NiO was obtained, and at higher Al_2O_3 contents only the diffraction pattern of Al_2O_3. However, we did not find any amorphous structures, and this enabled us to study both the phase composition and the crystallographic characteristics of the phases present in the catalysts, i.e., to do what appeared to be impossible according to [2]. It was of interest also to apply x-ray methods to check Milligan and Richardson's conclusion [3], based on magnetic measurements, to the effect that with increase in the Al_2O_3 content of the samples studied the dimensions of the NiO crystals diminish. In the investigations [2] and [3] the structural data are not compared with data on catalytic activity, and one of our main tasks in this investigation was therefore the filling of this gap.

EXPERIMENTAL

The catalysts investigated were prepared by the precipitation of mixtures of Al and Ni hydroxides with 10% ammonia from mixtures of 10% solutions of the nitrates (pH 8 at end of precipitation); the precipitates were washed, filtered off, molded in a standard manner, and dried at 110°; for each composition portions were roasted at 400°, 600°, and 750°; some were roasted at 900°. The NiO contents of the finished catalysts were determined by analysis (precipitation of Ni with dimethylglyoxime). It was found that the catalysts contained about 4, 9, 14, 20, 31, 40, 51, and 59 moles percent of NiO. Also, under the same conditions unmixed Al_2O_3 and NiO were prepared (denoted by 0 and 100, respectively). In the examination of the results obtained the samples will be denoted by a figure indicating the NiO content (moles %) with a subscript indicating the roasting temperature, e.g. 40_{600} is a catalyst containing 40 moles percent of NiO roasted at 600°.

The x-ray photographs were taken on Agfa Laue film in a powder camera capable of taking the diffraction pattern at Bragg angles of 15-55° with filtered (Ni filter) copper radiation (35 kv and 14 ma) at exposures of 18 to 20 hours. Photographs taken of a standard (MgO, a = 4.203 A) [4] showed that with variation in the angle of reflection the radius of the plate varied from 45.7 to 46.3 mm. The appropriate correction was introduced in the

TABLE 1

Relative Intensities of Lines on X-Ray Photographs and Interplanar Distances (A) in Crystalline Phases Present in the Catalysts

NiO content (mole %)	(pure Al_2O_3)		4		9		14		20	
Roasting temperature (° C)	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
400	сл	2,45	осл ср	2,89 2,40	ср	2,44	я	2,42	я	2,42
	срсл	1,97	ср осл	1,99 1,75	яср	1,99	я	2,00	я	2,00
			осл	1,53	осл	1,53	осл	1,55	оосл	1,55
	ср оосл	1,394 1,251	я оосл	1,400 1,251	я	1,402	я	1,404	я	1,407
							оосл	1,224	осл	1,222
	оосл	1,141	сл осл	1,134 1,025	сл осл	1,134 1,017	осл оосл	1,150 1,035	осл оосл	1,154 1,040
					осл	0,970	осл	0,990	оосл	0,990
600			оосл ср	2,86 2,40	осл я	2,82 2,41	осл я	2,92 2,41	осл я	2,82 2,41
			осл	2,40	оосл	2,31				
			ср осл	1,98 1,53	я осл	1,99 1,52	я осл	2,00 1,54	я осл	2,00 1,54
			я	1,399	я	1,400	я	1,402	я	1,406
					осл	1,221	оосл	1,217	оосл	1,217
			сл осл	1,135 1,023	осл	1,151	осл оосл	1,148 1,032	осл оосл	1,154 1,03
					осл	0,988	оосл	0,989	оосл	0,995
750	срсл	2,42	осл ср	2,83 2,40	осл я	2,78 2,41	осл я	2,82 2,41	сл я	2,87 2,41
			осл	2,30						
	ср	1,98	ср оосл	1,98 1,74	я	1,99	я	1,99	я	1,99
	срсл	1,56	осл	1,52	осл	1,53	сл	1,53	сл	1,54
	яср оосл	1,390 1,251	я	1,396	я	1,397	я	1,401	я	1,404
			осл	1,222	осл	1,223	осл	1,217	осл	1,216
	оосл	1,142	сл осл	1,134 1,021	осл осл	1,144 1,040	осл осл	1,142 1,028	осл оосл	1,151 1,034
					осл	0,988	осл	0,990	осл	0,990

Intensities (I): оя) very bright; я) bright; яср) moderately bright; ср) medium;

31		40		51		59		100 (pure NiO)		Phase and indices of lines
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	
осл	2,82									γ-Al_2O_3 (022)
оя	2,43	яср	2,46							γ-Al_2C_3 (113)
				срсл	2,42	срсл	2,42	яср	2,42	NiO (111)
						ср	2,09	я	2,09	NiO (002)
я	2,01	яср	2,03	срсл	2,04					γ-Al_2O_3 (004)
										γ-Al_2O_3 (024)
				оосл	1,56					γ-Al_2O_3 (333)
								яср	1,478	NiO (022)
я	1,414	я	1,420	срсл	1,425	срсл	1,467	срсл	1,260	γ-Al_2O_3 (044)
				оосл	1,252	срсл	1,425			γ-Al_2O_3 (026)
										NiO (113)
осл	1,210	осл	1,218			оосл	1,252	сл	1,205	γ-Al_2O_3 (335)
										NiO (222)
осл	1,159	осл	1,162	оосл	1,170	оосл	1,158	сл	1,042	γ-Al_2O_3 (444)
										γ-Al_2O_3 (355)
										NiO (004)
										γ-Al_2O_3 (008)
осл	2,85									γ-Al_2O_3 (022)
я	2,44	яср	2,44			осл	2,44			γ-Al_2O_3 (113)
				срсл	2,42	срсл	2,41	яср	2,42	NiO (111)
										γ-Al_2O_3 (222)
						ср	2,10	оя	2,09	NiO (002)
я	2,03	яср	2,03	ср	2,04					γ-Al_2O_3 (004)
осл	1,56	сл	1,56	оосл	1,56	срсл	2,04			γ-Al_2O_3 (333)
						сл	1,471	яср	1,478	NiO (022)
я	1,412	я	1,419	срсл	1,425	сл	1,425			γ-Al_2O_3 (044)
				оосл	1,257	осл	1,257	срсл	1,260	NiO (113)
осл	1,217	осл	1,227							γ-Al_2O_3 (335)
								сл	1,205	NiO (222)
осл	1,160	осл	1,162	оосл	1,162					γ-Al_2O_3 (444)
								осл	1,042	γ-Al_2O_3 (355)
										NiO (004)
										γ-Al_2O_3 (008)
осл	2,85	осл	2,82							γ-Al_2O_3 (022)
я	2,44	яср	2,46	ср	2,45	ср	2,45			γ-Al_2O_3 (113)
				сл	2,41	оосл	2,42	яср	2,43	NiO (111)
				осл	2,08	ср	2,11	оя	2,09	γ-Al_2O_3 (222)
										NiO (002)
я	2,02	яср	2,03	ср	2,02	срсл	2,04			γ-Al_2O_3 (004)
						оосл	1,18			γ-Al_2O_3 (024)
сл	1,54	осл	1,55	оосл	1,54	оосл	1,54			γ-Al_2O_3 (333)
				осл	1,464	срсл	1,475	яср	1,475	NiO (022)
я	1,410	я	1,419	ср	1,421	ср	1,423			γ-Al_2O_3 (044)
				оосл	1,257	осл	1,257	срсл	1,257	γ-Al_2O_3 (026)
										NiO (113)
осл	1,218	осл	1,218	оосл	1,217					γ-Al_2O_3 (335)
						осл	1,202	сл	1,204	NiO (222)
осл	1,155	осл	1,155	оосл	1,162	осл	1,166			γ-Al_2O_3 (444)
осл	1,043							осл	1,044	γ-Al_2O_3 (355)
										NiO (004)
осл	1,002									γ-Al_2O_3 (008)

срсл) moderately weak; сл) weak; осл) very weak; оосл) very very weak.

determination of the angle θ: from the graph for the relation of the coefficient K to the diameter of the diffraction rings L we determined its value ($K = \frac{45}{\pi R_{eff}}$), and hence the angle θ, equal to the product KL. The interplanar distances d, found from the reflection angles, are in this way determined accurately within ± 0.02 A for small angles (15-16°) and within 0.002 A for large angles (50-55°). The intensities I of the diffraction lines were estimated visually on an eight-grade scale; the relative intensities of the lines on each individual x-ray photograph were determined (the data in Table 1, therefore, cannot be used for the comparison of the same lines on different x-ray photographs).

The dimensions of the crystals were determined from the microphotometric curves obtained on an MF-4 for the (044) reflection of the spinel structure and the (022) reflection of the NiO. The calculation was carried out by the Seljakow-Scherrer formula $D = \frac{\lambda}{\beta \cos \theta}$ [in which β is the half-width (radians) of the diffraction line], a standard being used to exclude the geometric effect [5, 6]. If we assume that β was estimated accurately within 0.25 mm, then our determinations on the crystals (size in the range 100-120 A) were accurate within $\Delta D = \pm 5$ A.

Table 1 gives values of d and I found from x-ray photographs of catalysts roasted at 400°, 600°, and 750°, and the phases and plane indices to which the reflection data correspond are given. To economize space we do not give the analogous table for catalysts roasted at 900-1000°: the results obtained for these samples are in close accord with those given in Table 1; it must be added that, in these samples also, α-Al_2O_3 was not detected by phase analysis. The nature of the phases was judged a) by comparison of the photographs with those of γ-Al_2O_3 (defective spinel structure) and NiO (NaCl type) and b) from tabulated values of d and I for γ-Al_2O_3, NiO, and $NiAl_2O_4$ [5]. We must point out that, although the lines for which d is close to 2.43, 2.01, 1.55, or 1.42 A are attributed to the γ-Al_2O_3 phase in Table 1, they may with equal justification be attributed to reflections of $NiAl_2O_4$ (which, like γ-Al_2O_3, has a spinel structure, though a less defective one) or if its solid solution in Al_2O_3. In the x-ray photographs the NiO and Al_2O_3 lines differed in width: this criterion was used in the assignment of the line having d = 2.42 A (51_{400}, 59_{400}, 51_{600}) to the NiO phase, though in these cases there were no γ-Al_2O_3 lines having values of d close to 2.42 A.

Table 1 shows that crystalline catalysts were obtained at all NiO concentrations and at all temperatures. Table 2 gives the values found for the a parameters of crystal lattices of spinel and NiO structures, calculated from the (044) reflections in the first case and from (113) reflections in the second; these were used because 1) they are fairly intense; 2) they are formed at a fairly large reflection angle with resulting high accuracy of determination; and 3) neither of these reflections is close enough to others for measurements to be difficult or for it to be coincident with a reflection of the second phase. Measurements of a were made accurately within ± 0.02 A for the spinel structure, and within ± 0.01 A for NiO. The values found for the linear dimensions of the crystals of the two phases are given in Table 3.

DISCUSSION OF RESULTS

On examination of the results the first matter of note is the absence of amorphous products among the catalysts investigated. This does not vitiate the data presented at the beginning of this paper and the conclusions of Milligan and Merten [2], but supplements them. In fact, the conditions under which we prepared our precipitates were quite clearly different, which makes it possible to estimate the effect on the state of the catalyst of two factors, genetic (precipitation conditions) and concentrational (proportions of components, "mutual protection"). Our results [1], including those obtained with catalysts containing 51 and 59 moles percent of NiO, i.e., with those corresponding to the zone of amorphous structures, showed that precipitation conditions have a greater effect on the state of the catalyst than the proportions of its components, i.e., that the genetic conditions constitute a more powerful factor than the "mutual protective action".

The second important result of the x-ray structure measurements carried out in this investigation was the proof (Tables 1 and 2) that catalysts containing less than 50 moles percent of NiO roasted at any of the temperatures used in the experiments do not contain NiO as a separate phase and are, from the point of view of x-ray diffraction, one-phase systems. This is highly consistent with data on selectivity [1]: all these catalysts, with the exception of 40_{400}, 40_{600}, and 40_{750} (on which dehydrogenation occurred to a slight extent), only dehydrated

$i\text{-}C_3H_7OH$. Catalysts containing more than 50 moles percent of Ni containing nickelous oxide as a crystalline phase, and the appearance of this phase is associated with change in selectivity [1].

TABLE 2

Lattice Parameter a (A)

NiO content (mole %)	Roasting temperature (°C)			
	400	600	750	900
Spinel structure				
0	7,89	—	7,87	7,85*
4	7,92	7,91	7,90	7,87
9	7,93	7,92	7,91	7,91
14	7,95	7,93	7,93	—
20	7,96	7,95	7,95	7,95
31	8,00	7,99	7,98	7,98
40	8,03	8,03	8,03	7,99
51	8,06	8,06	8,04	8,03
59	8,06	8,06	8,05	8,05
NiO				
51	—	—	4,17	4,17
59	—	4,17	4,17	4,17
100	4,18	4,18	4,17	4,17*

* This sample was roasted at 1000°.

TABLE 3

Linear Dimensions of Crystals (A)

NiO content (mole %)	Roasting temperature (° C)			
	400	600	750	900
Spinel structure				
	40	—	55	65*
4	55	65	70	100
9	55	55	85	95
14	60	65	85	—
20	50	55	65	110
31	45	50	65	120
40	65	70	85	120
51	—**	—**	90	190
59	—**	—**	110	220
NiO				
51	—	—	100	160
59	—	—	110	220
100	220	550	900	2500*

* The catalyst was roasted at 1000°.

** The dimensions of the crystals were not determined because of the merging of the NiO and spinel-structure lines.

Table 2 gives data of great importance in the determination of the nature of the single phase of which catalysts containing less than 50 moles percent of NiO are made up; these data show that with increase in the NiO content the value of a for the spinel structure increases approximately linearly from 7.89 A ($Al_2O_{3\,400}$), 7.87 A ($Al_2O_{3\,600}$), and 7.85 A ($Al_2O_{3\,750}$) to 8.05 and 8.06 A for catalysts with 51 moles percent of NiO, and with further increase in NiO concentration to 59 moles percent it does not change. Hence, the limit in the increase of a is attained when the components are in equimolecular proportions. It is known, however, that for $\gamma\text{-}Al_2O_3$ a = 7.85-7.89 A [7] and for $NiAl_2O_4$ a = 8.05 A [8].

Thus, the observed linear change of a with increase in NiO concentration shows that the one-phase catalyst is formed by the incorporation of NiO in the defective spinel lattice of $\gamma\text{-}Al_2O_3$; this gives, without change in the type of lattice, solid solutions which are essentially solutions of the spinel $NiAl_2O_4$ in excess of $\gamma\text{-}Al_2O_3$. As already pointed out in the previous paper [1], the formation of a spinel in the thermal treatment of mixtures of hydroxides is the result of intermolecular dehydration of $Ni(OH)_2$ and AlOOH or $Al(OH)_3$: the results show that this process proceeds readily already at 400°.

The appearance of the second phase, free NiO, corresponds to the completion of the formation of the spinel $NiAl_2O_4$. The fact that this phase appears without distortion of the lattice parameter of the spinel (Table 2, 51_{400}, 51_{600}, 59_{400}, 59_{600}) casts doubt on the assertion [2] that NiO is soluble in $NiAl_2O_4$: if it is considered that for dissolution roasting for seven hours at 400°, or 600° is inadequate, then at 750°, and certainly at 900°, it should be sufficient. Hence, if NiO does dissolve in $NiAl_2O_4$, then it dissolves to a limited extent, or very slowly.

The changes in dispersity that we observed in the system $NiO\text{—}Al_2O_3$ were in general the same as those found in the magnetochemical investigation [3]. With increase in NiO content the linear dimensions of the crystals increase, as will be seen from Table 3. However, this increase is nonlinear. A maximum is observed in the region of NiO contents from 5 to 15 moles percent. It is just this range of NiO concentrations that corresponds to maximum specific activity [1]. We consider that this observation of a correspondence between this maximum region in the relation between crystal size and composition and the maximum in the relation between activity and size is in accord with general considerations [9, 10], relating to the effect of dispersity on activity: maximum activity does not correspond to the finest crystals.

Until now, we have discussed the effect of catalyst composition on structure. We must examine also the effect of thermal treatment. It is to be expected that the higher the roasting temperature, the greater the dimensions of the crystals (Table 3), because the rate of sintering increases with rise of temperature. Some reduction in the value of d (Table 1) and also in the value of a in catalysts containing 4-31 moles percent of NiO with rise in roasting temperature indicates that sintering is accompanied by increase in order in the crystal lattice.

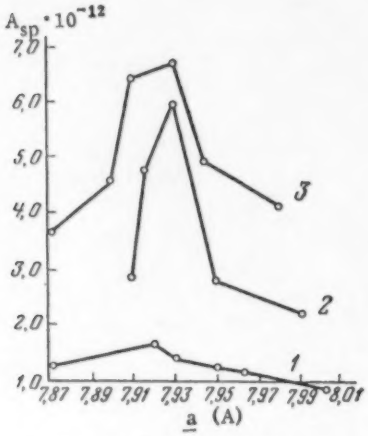

Fig. Effect of change in interatomic distances in the spinel-type lattice on the specific dehydrating activity of $NiO-Al_2O_3$ catalysts (NiO not greater than 50 moles percent at 245°. Temperatures of roasting of catalysts: 1) 400°, 2) 600°, 3) 750°; a is the lattice parameter for the spinel structure.

In connection with these observations it is of interest to examine the effect of changes of a on the activities of catalysts of NiO content less than 50%, whose one-phase character was proved above. It was shown in [1] that the optimum composition corresponding to maximum activity in the dehydration reaction was 5-15 moles percent of NiO: the specific activity A_{sp} was here expressed as the number of molecules reacting per m^2 of surface per second. As this optimum A_{sp} is preserved at all temperatures of catalysis experiments in the range 230-290°, in the figure we have presented a picture, which may be regarded as typical for this work, of the relation of A_{sp} to a for experiments at 245°. The graph shows that catalysts containing 4-15 moles percent of NiO (a = 7.91-7.93 A) are more active than pure Al_2O_3, and that change in the value of a has a great effect on activity. For the dehydration of $i\text{-}C_3H_7OH$ optimum a corresponds to the optimum with respect to composition. As the catalysts under discussion are one-phase systems and their activities are therefore the same in nature, the results show the effect of the geometric factor in a fairly clear form: the most favorable interatomic distances in the catalyst lattice for the arrangement of the alcohol molecule undergoing dehydration (the group $CHOH-CH_3$) on the surface of the catalyst are attained at a = 7.90-7.95 A. It will be obvious that, apart from the effect of the purely geometric factor, an important part may be played here by change in the electronic state of the catalyst resulting from change in NiO concentration, but we have not studied this factor and have no means of assessing the magnitude of its effect. As regards the variation of a with composition and the corresponding changes in activity, these conform closely with the views developed by the multiplet theory of catalysis [11] and also with the conclusions and schemes in the papers [12, 13] relating to the effect of a on activity. An important difference in the basis of the conclusions relating to the relation of A_{sp} to a given in the present paper from that given in the papers [12, 13] lies in the fact that in the present work the effect of surface area on activity is excluded in that A_{sp} characterizes the activity of 1 m^2 of surface.

We conclude that there is complete agreement between the results obtained in the characterization of $NiO-Al_2O_3$ catalysts by chemical and x-ray methods in the present investigation and in [1].

SUMMARY

An x-ray investigation was made of coprecipitated (pH 8) $NiO-Al_2O_3$ catalysts containing 0-100 moles percent of NiO and of the structural changes occurring in them when submitted to various thermal treatments in the range 400-900°.

1. Unlike catalysts described in [2], all the catalysts prepared under the conditions indicated are crystalline. It was shown, therefore, that the conditions of preparation affect the structure of the catalysts to a greater extent than the quantitative proportions of components.

2. Catalysts containing less than 50 moles percent of NiO are one-phase systems and do not contain free NiO. By measurement of the parameter of the crystal lattice and its variation with NiO concentration it was shown that these one-phase catalysts consist of solutions of the spinel $NiAl_2O_4$ in excess of $\gamma\text{-}Al_2O_3$.

3. The results of phase and structural analysis were compared with the catalytic properties of $NiO-Al_2O_3$ [1]: it was shown that there are optimum spinel lattice parameters for dehydration in the range 7.90-7.95 A.

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REVERSE-DISPROPORTIONATION REACTION OF CHELATE ZIRCONIUM COMPOUNDS

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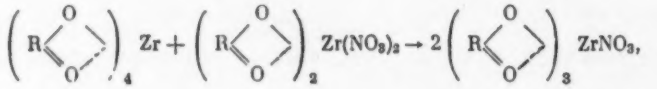
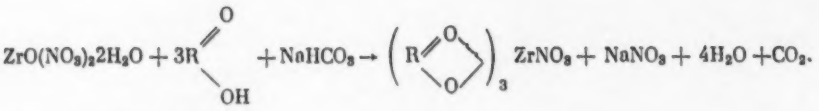
In a previous communication [1] we described some exchange reactions of chelate zirconium compounds. In the double decompositions of zirconium tetrakisacetylacetonate with benzoylacetone, acetoacetic ester, and salicylaldehyde, the zirconium retains the coordination number of eight. Exchange reactions occur also in cases in which there is a change of coordination number. This happens in the conversion of zirconium tetrakisacetylacetonate and tetrakisbenzoylacetonate into the corresponding monochlorides by acetyl chloride and in the conversion of zirconium tetrakisacetylacetonate into alkyl orthozirconates under the action of alcohols.

In the present paper we describe other reactions of this type. The most interesting of them is a reaction of reverse disproportionation, the examples examined being reaction between zirconium tetrakisacetylacetonate and zirconium bisacetylacetonate dinitrate and reaction between zirconium tetrakisacetylacetonate and zirconium bisbenzoylacetonate dinitrate. The reactions went according to the scheme:



in which is the acetylacetone (2,4-pentanedione) or benzoylacetone (1-phenyl-1,3-butanedione) residue. Analogous reverse-disproportionation reactions have been described by us [2, 3] for orthotitanic esters and alkoxyhalotitaniums and by British chemists [4] for alkyl orthozirconates and alkoxyhalozirconiums. Such reactions are unknown for chelate compounds.

To provide proof of structure zirconium trisacetylacetonate nitrate and zirconium trisbenzoylacetonate nitrate were prepared by the reaction of zirconyl nitrate with the corresponding β-diketones in presence of sodium bicarbonate:



The choice of the dinitrates of the zirconium chelates in the study of the above-mentioned reactions was determined by the fact that the preparation of the corresponding dichlorides presents some difficulty due to their instability to heat and to atmospheric moisture. Thus, it has been stated [5, 6] that zirconium bisacetylacetonate dichloride and zirconium bisbenzoylacetonate dichloride can be prepared by reaction between β-diketones and $ZrCl_2$ only in a medium of dry ether with careful avoidance of overheating; replacement of ether by benzene or chloroform always leads to the formation of the corresponding monochlorides. Moreover, like zirconium tetrachloride, the dichlorides are difficult to purify.

We found that zirconium bisacetylacetonate dinitrate and zirconium bisbenzoylacetonate dinitrate can be prepared by reaction of zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$ with the β-diketones in a benzene or chloroform medium and that they are readily purified by recrystallization from various organic solvents. On the basis of the

reaction between zirconium bisacetylacetonate dinitrate and benzoylacetone, taken as a typical example, it was shown that new dinitrates of this type can be prepared by exchange reaction with β-diketones.

The resulting mono- and di-nitrates of zirconium chelates are colorless crystalline compounds, soluble in benzene, dioxane, chloroform, and toluene; from such solutions stable compounds of the following compositions were isolated: $[(C_5H_7O_2)_2Zr(NO_3)_2]_2C_6H_6$; $[(C_{10}H_9O_2)_3ZrNO_3]_2C_6H_6$; $[(C_{10}H_9O_2)_3ZrNO_3]_2 \cdot C_4H_8O_2$. The nitrates also form double compounds with chloroform which were not investigated further. Although the nitrates studied were prepared from zirconyl nitrate containing two molecules of water of crystallization, they are unstable to the action of moisture. Thus, in an attempt to recrystallize zirconium bisacetylacetonate dinitrate from water, with heating to not above 50°, we obtained a hydrolysis product in which only one-third of the acetylacetonate residues of the original compound were retained.

EXPERIMENTAL

Zirconium Bisacetylacetonate Dinitrate $(C_5H_7O_2)_2Zr(NO_3)_2$

Dry benzene (250 ml) was poured on 26.7 g (0.1 mole) of zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$, and 20 g (0.2 mole) of acetylacetone (2,4-pentanedione) was added. The mixture was heated for two hours. It was filtered, solvent was distilled off under reduced pressure, and the residue was recrystallized from benzene; yield 16.9 g (41 %); m. p.* 146-147.5°.

Found %: C 34.85, 34.97; H 3.74, 3.72; Zr 20.25, 20.52; N 6.16, 5.98. $[(C_5H_7O_2)_2Zr(NO_3)_2]_2C_6H_6$. Calculated %: C 34.49; H 3.78; Zr 20.17; N 6.19.

The product was heated for five hours at 50-60° and 1 mm and was analyzed; m. p. 146-148°.

Found %: C 29.35, 29.14; H 3.50, 3.74; Zr 21.95, 22.61. $(C_5H_7O_2)_2Zr(NO_3)_2$. Calculated %: C 29.03; H 3.41; Zr 22.07.

Zirconium Bisbenzoylacetonate Dinitrate $(C_{10}H_9O_2)_2Zr(NO_3)_2$

A mixture of 13.3 g (0.05 mole) of zirconyl nitrate and 16.2 g (0.1 mole) of benzoylacetone (1-phenyl-1,3-butadione) was heated in dry chloroform (100 ml) for 3.5 hours. The precipitate was filtered off, solvent was distilled off from the clear filtrate, and the residue was crystallized from chloroform. The product formed clear crystals, m. p. 185-186°; yield 12.2 g (45%).

Found %: C 44.70, 44.50; H 3.62, 3.57; Zr 17.34, 17.16. $(C_{10}H_9O_2)_2Zr(NO_3)_2$. Calculated %: C 44.66; H 3.37; Zr 16.98.

Reaction of Zirconium Bisacetylacetonate Dinitrate With Benzoylacetone

To a melt of 3.2 g (0.02 mole) of benzoylacetone, 4.5 g (0.01 mole) of zirconium bisacetylacetonate dinitrate $[(C_5H_7O_2)_2Zr(NO_3)_2]_2C_6H_6$ was added. The mixture was heated at 100° for two hours, and the acetylacetone formed was vacuum-distilled off; benzene was added to the reaction mixture and distillation was continued until the mixture was completely freed from acetylacetone and solvent. The yield of zirconium bisbenzoylacetonate dinitrate was quantitative. After being recrystallized from benzene and heated for 4.5 hours at 50-60° and 2 mm to remove combined benzene, the substance melted at 185-186°.

Found %: C 44.44, 44.58; H 3.31, 3.49; Zr 17.08, 17.40.

Zirconium Trisacetylacetonate Nitrate $(C_5H_7O_2)_3ZrNO_3$

Preparation from zirconyl nitrate. A mixture of 2.67 g (0.01 mole) of zirconyl nitrate $ZrO(NO_3)_2 \cdot 2H_2O$, 3.0 g (0.03 mole) of acetylacetone, and 0.84 g (0.01 mole) of sodium bicarbonate was heated in a benzene medium

* When samples of zirconium bisacetylacetonate dinitrate and other substances described below were heated in sealed capillaries, gradual changes occurred in the sample over a wide temperature range; the melting points given are the temperatures at which the samples were converted into clear liquids.

(15 ml) for 14 hours at 80-90° (until bubbles of CO_2 ceased to separate). The reaction mixture was filtered, and solvent was distilled from the filtrate. The solid residue was recrystallized from benzene; yield 1.07 g (22%); m. p. 145-147°.

Found %: C 39.92, 39.71; H 4.97, 4.54; Zr 20.13, 20.72; N 3.14, 3.17. $(C_5H_7O_2)_3ZrNO_3$. Calculated %: C 39.97; H 4.69; Zr 20.26; N 3.10.

Preparation from zirconium bisacetylacetonate dinitrate. A mixture of 4.13 g (0.01 mole) of zirconium bisacetylacetonate dinitrate, 1.0 g (0.01 mole) of acetylacetone, and 0.84 g (0.01 mole) of sodium bicarbonate was heated in a benzene medium (30 ml) at 70-80° until bubbles of CO_2 ceased to separate (four hours). Solvent was distilled from the clear filtrate; the weight of crude product was 3.83 g (85%). After being crystallized from benzene the product melted at 145-149°.

Found %: C 39.80, 39.86; H 4.63, 4.59; Zr 20.69, 20.41.

Reaction Between Zirconium Tetrakisacetylacetonate and Zirconium Bisacetylacetonate Dinitrate

A benzene solution of 2.06 (0.02 mole) of zirconium bisacetylacetonate dinitrate was added to a solution of 2.43 g (0.02 mole) of zirconium tetrakisacetylacetonate in 4 ml of benzene. The reaction mixture was heated for three hours. Solvent was vacuum-distilled off, and the residue was crystallized from benzene; yield 1.93 g (43%). After two recrystallizations from benzene the product melted at 145-147° and corresponded in analysis to zirconium trisacetylacetonate nitrate.

Found %: C 39.82, 39.78; H 4.68, 4.69; Zr 20.69, 20.71; N 3.29, 3.17.

Zirconium Trisbenzoylacetonate Nitrate $(C_{10}H_9O_2)_3ZrNO_3$

Preparation from zirconyl nitrate. Chloroform (25 ml) was poured on a mixture of 2.67 g (0.01 mole) of zirconyl nitrate, 4.86 g (0.03 mole) of benzoylacetone, and 0.84 g (0.01 mole) of sodium bicarbonate. The reaction mixture was heated at 60-70° until the separation of CO_2 bubbles stopped (20 hours). Solvent was distilled from the clear filtrate. The residue was crystallized from chloroform; yield 1.9 g (30%). The product was recrystallized from chloroform and then heated for 11 hours at 50-60° and 10^{-4} mm; the substance still contained traces of chlorine (Beilstein test).

Found %: C 56.55, 56.37; H 4.61, 4.24; Zr 14.31, 14.31. $(C_{10}H_9O_2)_3ZrNO_3$. Calculated %: C 56.60; H 4.47; Zr 14.34.

Part of the product was recrystallized from benzene; m. p. 133-135°.

Found %: C 58.85, 58.96; H 4.47, 4.56; Zr 13.13, 13.42. $[(C_{10}H_9O_2)_3ZrNO_3]_2C_6H_6$. Calculated %: C 58.63; H 4.47; Zr 13.50.

The product was unchanged after being heated in a vacuum for many hours.

Reaction Between Zirconium Tetrakisbenzoylacetonate and Zirconium Bisbenzoylacetonate Dinitrate

A mixture of 1.0 g (0.0013 mole) of zirconium tetrakisbenzoylacetonate, 0.73 g (0.0013 mole) of zirconium bisbenzoylacetonate dinitrate, and 10 ml of benzene was heated for 6.5 hours at 85-90°, and solvent was then distilled off under reduced pressure. Crystallization of the residue from benzene gave 1.05 g (55%) of product, m. p. 132°. In composition the product corresponded to zirconium trisbenzoylacetonate nitrate with combined benzene $[(C_{10}H_9O_2)_3ZrNO_3]_2C_6H_6$. Part of the product was recrystallized from dioxane; m. p. 125-126°.

Found %: C 56.51, 56.42; H 4.74, 4.59; Zr 13.54, 13.59. $[(C_{10}H_9O_2)_3ZrNO_3]_2C_4H_8O_2$. Calculated %: C 56.47; H 4.59; Zr 13.41.

Another part of the product was recrystallized from toluene; m. p. 152-153.5°.

Found %: C 56.28, 56.28; H 4.24, 4.34; Zr 14.44, 14.44; N 2.12. $(C_{10}H_9O_2)_3ZrNO_3$. Calculated %: C 56.60; H 4.47; Zr 14.34; N 2.20.

SUMMARY

1. By reaction of β-diketones with zirconyl nitrate, zirconium bisacetylacetonate dinitrate and zirconium bisbenzoylacetonate were prepared.

2. By reaction of β-diketones with zirconyl nitrate in presence of sodium bicarbonate, zirconium trisacetylacetonate nitrate and zirconium trisbenzoylacetonate nitrate were prepared.

3. The reverse-disproportionation reaction is applicable to chelate zirconium compounds. Reaction of zirconium tetrakisacetylacetonate and of zirconium tetrakisbenzoylacetonate with the corresponding dinitrates gave the zirconium trisacylacetonate mononitrates.

4. The above-mentioned mono- and di-nitrates give double compounds with benzene and dioxane.

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SYNTHESIS AND INVESTIGATION OF THE PROPERTIES OF LIQUID α, α, α, ω, ω, ω-HEXAMETHYLPOLY [(ANILINOMETHYL)METHYL] POLYSILOXANES

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Liquid polyorganosiloxanes containing both like and different organic groups on each silicon atom have been described in the literature. The most detailed study has been devoted to liquid polydimethylsiloxanes both of cyclic structure, and also of linear structure with terminal trimethylsilyl groups. There is only a little information in the literature on liquid organosilicon polymers in which the organic side chains contain polar groups. Speier [1] has described liquid polymers containing chlorine in the methyl group both on silicon atoms in the chain and on terminal silicon atoms.

Andrianov and Odinets [2] prepared liquid organosilicon polymers of various degrees of polymerization containing 1,2, and 3 chlorine atoms in the phenyl group and with terminal trimethylsiloxy groups. Sommer [3, 4] prepared liquid organosilicon polymers containing dimethylsiloxane repeating units and terminal ether groups. The only liquid organosiloxanes containing nitrogen in the organic group that have been synthesized are bisaminomethyltetramethylsiloxane [5] and (aminomethyl)heptamethylcyclotetrasiloxane [6].

The synthesis of liquid polyorganosiloxanes containing amine nitrogen in the silicon-attached organic group is not only of theoretical interest (it permits the study of the effect of amine nitrogen on the properties of liquid polymers), but may lead to the preparation of polymeric liquids having valuable technical properties. In the present paper we describe liquid organosilicon polymers containing nitrogen in the groups attached to chain silicon atoms and having terminal trimethylsiloxy groups. The synthesis of these polymers was carried out by the cohydrolysis of ethoxytrimethylsilane with various N-substituted (diethoxymethylsilyl)methylamines:

$$2n\,(CH_3)_3SiOC_2H_5 + n\,CH_3(XCH_2)Si(OC_2H_5)_2 + 4nH_2O \rightarrow$$
$$\rightarrow (CH_3)_3SiO\left[\begin{matrix}CH_3\\|\\Si-O\\|\\CH_2X\end{matrix}\right]_n Si(CH_3)_3 + 4nC_2H_5OH,$$

in which

$$X = C_6H_5NH;\ ClC_6H_4NH;\ C_2H_5C_6H_5N;\ (C_2H_5)_2N.$$

Polymers having n = 1,2, and 3 were obtained.

Hydrolysis of ethoxy [(o-chloroanilino)methyl]dimethylsilane gave bis[(o-chloroanilino)methyl]tetramethyldisiloxane:

$$ClC_6H_4NHCH_2(CH_3)_2SiOC_2H_5 + H_2O \rightarrow [ClC_6H_4NHCH_2Si(CH_3)_2]_2O + 2C_2H_5OH.$$

We studied also the replacement of chlorine by the anilino group in 3-(chloromethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane:

$$(CH_3)_3SiO-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2Cl}{|}}{Si}}-OSi(CH_3)_3 + 2C_6H_5NH_2 \rightarrow (CH_3)_3SiOSi\left(\begin{matrix}CH_2NHC_6H_5\\|\\-O-Si(CH_3)_3\\|\\CH_3\end{matrix}\right) + C_6H_5NH_2\cdot HCl.$$

In the study of this reaction it was shown that replacement of the halogen of the chloromethyl group in 3-(chloromethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane proceeds with greater difficulty than in the reaction of aniline with (chloromethyl)diethoxymethylsilane. The reaction of aniline with 3,5-bischloromethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane is still more difficult, and in this case we did not succeed in isolating pure 3,5-bisanilinomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane.

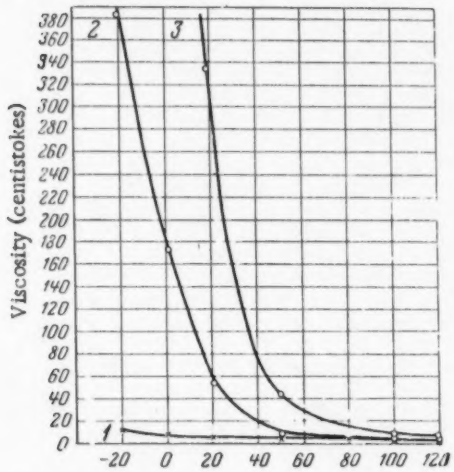

Fig. 1. Temperature-dependence of viscosity for $(CH_3)_3SiO[Si(CH_2NHC_6H_5)(CH_3)-O]_nSi(CH_3)_3$

1) n = 1; 2) n = 2; 3) n = 3.

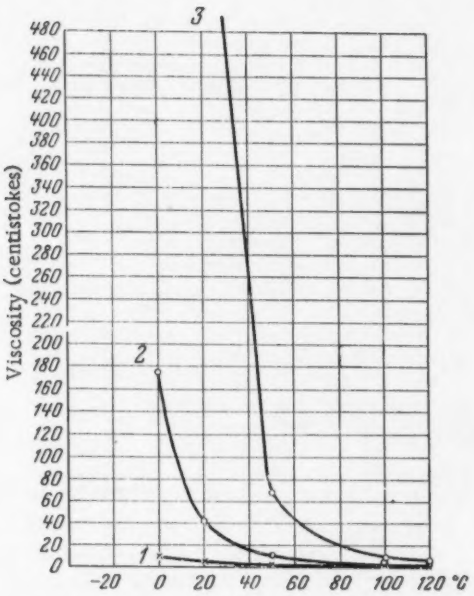

Fig. 2. Temperature-dependence of viscosity for $(CH_3)_3SiO[Si(CH_2NC_2H_5C_6H_5)(CH_3)-O]_nSi(CH_3)_3$: 1) n = 1; 2) n = 2; 3) n = 3.

The physical properties of the new compounds prepared by these reactions are given in the table. The viscosities of the new compounds were studied. Figure 1 represents the temperature-dependence of viscosity for α, α, α, ω, ω, ω,-hexamethylpoly[(anilinomethyl)methyl] polysiloxanes. It will be seen that with increase in the degree of polymerization the temperature-dependence of viscosity increases greatly; thus when n = 1 the viscosity increases from 1.15 centistokes at 120° to 13 at − 20°, and when n = 3 it increases from 6.8 at 120° to 1771 at 0°. There is a great increase of the activation energy for viscous flow with increase in molecular weight. The introduction of one $[SiCH_3CH_2NHC_6H_5O]$ unit in the molecular chain increases the activation energy by about 3 kcal/mole.

Figure 2 shows the temperature-dependence of viscosity for α, α,α,ω,ω,ω-hexamethylpoly[(N-ethylanilinomethyl)methyl] polysiloxanes. The general picture is the same as in the previous case. The ethyl group has almost no effect. Figure 3 shows the temperature-dependence of viscosity for α,α,α,ω,ω,ω-hexamethylpoly[(o-chloroanilinomethyl)methyl] polysiloxanes. The introduction of chlorine into the phenyl group has a small effect on the temperature dependence of viscosity and increases the activation energy somewhat (as compared with the unsubstituted phenyl compound).

Figure 4 shows the temperature-dependence of viscosity for α,α,α,ω,ω,ω-hexamethylpoly[(diethylaminomethyl)methyl] polysiloxanes. In this case the introduction of one $[SiCH_3CH_2N(C_2H_5)_2O]$ unit into the molecular chain increases the activation energy for viscous flow by about 0.6 kcal/mole. The temperature-dependence of viscosity does not increase so greatly with increase in degree of polymerization as in the case of the anilino polymers. Thus, when n = 1 the viscosity increases from 0.85 centistoke at 120° to 7.2 at − 20°, and when n = 3 it increases from 1.82 at 120° to 51.3 at − 20°.

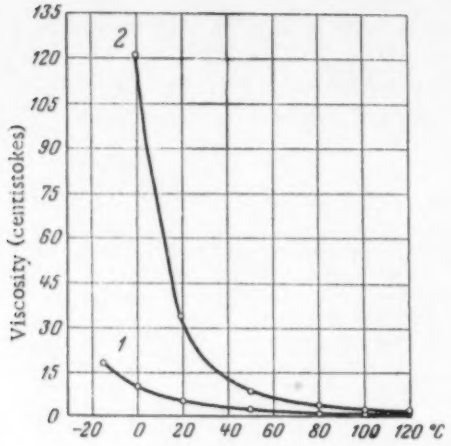

Fig. 3. Temperature-dependence of viscosity for $(CH_3)_3SiO[Si(CH_2NHC_6H_4Cl)(CH_3)-O]_nSi(CH_3)_3$: 1) n = 1; 2) n = 2.

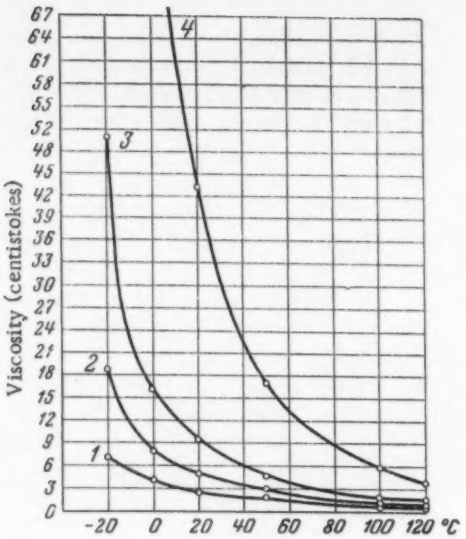

Fig. 4. Temperature-dependence of viscosity for $(CH_3)_3SiO[Si(CH_2N(C_2H_5)_2)(CH_3)-O]_nSi(CH_3)_3$: 1) n = 1; 2) n = 2; 3) n = 3; 4) n = 4.

For nonpolar liquid polymers the activation energy increases comparatively little with increase in molecular weight. Thus, for polymethylsiloxanes the activation energy increases from 2.2 kcal/mole for octamethyltrisiloxane to 3.01 kcal/mole for octadecamethyloctasiloxane [7]. The experimental results show that the activation energy for viscous flow is greatly dependent on the chemical composition of the group introduced into the methyl side chain.

EXPERIMENTAL

The following substances were used in this work:

1) $C_6H_5NHCH_2CH_3Si(OC_2H_5)_2$; b. p. 142-143° (10 mm), $n^{20}D$ 1.4978; d^{20}_4 1.004; 2) $C_6H_5(C_2H_5)NCH_2CH_3Si(OC_2H_5)_2$; b. p. 119-121° (2 mm); $n^{20}D$ 1.4990, d^{20}_4 0.9936; 3) $(C_2H_5)_2NCH_2CH_3Si(OC_2H_5)_2$, b. p. 52-54° (2 mm), $n^{20}D$ 1.4210, n^{20}_4 0.877; 4) o-$ClC_6H_4NHCH_2CH_3Si(OC_2H_5)_2$, b. p. 141-148° (6 mm), $n^{20}D$ 1.5115, d^{20}_4 1.087; 5) o-$ClC_6H_4NHCH_2(CH_3)_2SiOC_2H_5$, b. p. 132-133° (6 mm), $n^{20}D$ 1.5050, d^{20}_4 1.096; 6) $(CH_3)_3SiOC_2H_5$, b. p. 75°, $n^{20}D$ 1.3740, d^{20}_4 0.7535; 7) $(CH_3)_3SiO[SiCH_3(CH_2Cl)O]Si(CH_3)_3$, b. p. 96-102° (32 mm), $n^{20}D$ 1.4080, d^{20}_4 0.926; 8) $(CH_3)_3SiO[SiCH_3CH_2ClO]_2Si(CH_3)_3$, b. p. 150-160° (32 mm), $n^{20}D$ 1.4220, d^{20}_4 1.000.

Preparation of α,α,α,ω,ω,ω-Hexamethylpoly[(anilinomethyl)methyl]polysiloxanes $(CH_3)_3SiO[SiCH_2NHC_6H_5CH_3O]_nSi(CH_3)_3$

A mixture of 47 g (0.2 mole) of (anilinomethyl)diethoxymethylsilane and 59 g (0.5 mole) of ethoxytrimethylsilane was added over a period of one hour with stirring to 100 g of 0.1 N NaOH at 60-70° in a three-necked flask. The mixture was then stirred at 60-70° for five hours. The aqueous layer was separated, and the organosilicon layer was washed with distilled water until the reaction for OH^- was negative. It was dried in a desiccator over alkali and vacuum-distilled. The fractionation gave:

1) 12.8 g of a product of b. p. 136-140° (4 mm), $n^{20}D$ 1.4650, $d^{20}D$ 0.9436, which was found to be 3-(anilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane;

Found %: C 51.0, 50.9; H 8.9, 9.0; Si 24.1, 25.1; N 4.38, 4.9. $C_{14}H_{29}O_2Si_3N$. Calculated %: C 51.38; H 8.87; Si 25.65; N 4.28.

Found M 324; Calculated M 327.

TABLE

Name of substance	Formula of substance	B. p. in °C (p in mm)	F. p. (°C)	n_D^{20}	d_4^{20}	MR found	MR calc.	E_{act} for viscous flow +20—120° C (kcal/mole)
3-(Anilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane	$(CH_3)_3SiO\underset{\displaystyle CH_2NHC_6H_5}{\underset{\displaystyle \vert}{Si}}-O-Si(CH_3)_3$ $\vert$ CH_3	159—161 (22) 136—140 (4)	—93	1,4650	0,9439	95,8	96,14	3,348
3,5-Bisanilinomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_2NHC_6H_5}{\underset{\displaystyle \vert}{Si}}-O]_2Si(CH_3)_3$ $\vert$ CH_3	187—196 (3) 218—219 (5)	—60	1,5050	1,028	142,2	142,0	6,425
3,5,7-Trisanilinomethyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_2NHC_6H_5}{\underset{\displaystyle \vert}{Si}}-O]_3Si(CH_3)_3$ $\vert$ CH_3	281—283 (5)	—29	1,5220	1,073	189,46	186,7	9,213
3-(N-Ethylanilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane	$(CH_3)_3SiO\underset{\displaystyle CH_2NC_2H_5C_6H_5}{\underset{\displaystyle \vert}{Si}}-OSi(CH_3)_3$ $\vert$ CH_3	141—144 (4)	—73	1,4745	0,9416	105,9	104,9	3,304
3,5-Bis(N-ethylanilinomethyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_2NC_2H_5C_6H_5}{\underset{\displaystyle \vert}{Si}}-O]_2Si(CH_3)_3$ $\vert$ CH_3	230—235 (3)	—44	1,5065	1,015	160,6	161,0	6,203
3,5,7-Tris(N-ethylanilinomethyl)-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_2NC_2H_5C_6H_5}{\underset{\displaystyle \vert}{Si}}-O]_3Si(CH_3)$ $\vert$ CH_3	275—284 (1)	—20	1,5487	1,083	217,6	217,08	10,83

TABLE (Continued)

Name of substance	Formula of substance	B. p. in ° C (p in mm)	F. p. (° C)	n_D^{20}	d_4^{20}	MR found	MR calc.	E_{act} for viscous flow +20 – 120° C (kcal/mole)
3-(Diethylaminomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane	$(CH_3)_3SiO\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2N(C_2H_5)_2}{\overset{|}{\underset{|}{Si}}}}-O-Si(CH_3)_3$	68—71 (3)	Below —100	1,4128	0,8561	89,35	89,88	2,626
3,5-Bisdiethylaminomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2N(C_2H_5)_2}{\overset{|}{\underset{|}{Si}}}}-O]_2Si(CH_3)_3$	115—130 (3)	—93	1,4205	0,8909	129,8	130,85	3,195
3,5,7-Trisdiethylaminomethyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2N(C_2H_5)_2}{\overset{|}{\underset{|}{Si}}}}-O]_3Si(CH_3)_3$	150—160 (1)	—85	1,4280	0,905	169,7	171,87	3,829
3,5,7,9-Tetrakisdiethylaminomethyl-1,1,1,3,5,7,9,11,11,11-decamethylhexasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2N(C_2H_5)_2}{\overset{|}{\underset{|}{Si}}}}-O]_4Si(CH_3)_3$	205—215 (1)	—65	1,4390	0,9659	201,9	212,9	5,39
3-(o-Chloroanilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane	$(CH_3)_3SiO\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NHC_6H_4Cl}{\overset{|}{\underset{|}{Si}}}}-OSi(CH_3)_3$	147—150 (3)	—78	1,4752	1,002	101,7	102,07	3,526
3,5-Bis(o-chloroanilinomethyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane	$(CH_3)_3SiO[\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2NHC_6H_4Cl}{\overset{|}{\underset{|}{Si}}}}-O]_2Si(CH_3)_3$	208—215 (1)	—36	1,513	1,097	153,8	155,26	7,12
1,3-Bis(o-chloroanilinomethyl)-1,1,3,3-tetramethyldisiloxane	$[ClC_6H_4NHCH_2(CH_3)_2Si]_2O$	222—224 (5)	—	1,5425	1,1265	115,52	115,45	—

2) 7.7 g of a product of b. p. 187-196° (3 mm), $n^{20}D$ 1.5050, d^{20}_4 1.028, which was found to be 3,5-bisanilinomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane;

Found %: C 52.35, 52.71; H 7.89, 7.85; Si 21.2, 21.3; N 5.83, 5.74. $C_{22}H_{40}Si_4O_3N_2$. Calculated %: C 53.65; H 8.13; Si 22.76; N 5.69.

Found M 483; Calculated M 492.

The still residues from three experiments were combined and fractionated. This gave 6.3 g of 3,5-bisanilinomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, b. p. 218-219° (5 mm), $n^{20}D$ 1.5046, d^{20}_4 1.025 and 11.3 g of 3,5,7-trisanilinomethyl-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane, b. p. 181-183° (5 mm), $n^{20}D$ 1.5220; d^{20}_4 1.073.

Found %: C 53.26, 53.4; H 7.61, 7.89; Si 20.56, 20.76; N 6.14, 6.11. $C_{30}H_{51}Si_5O_4N_3$. Calculated %: C 54.89; H 7.76; Si 21.35; N 6.39.

Found M 653; Calculated M 657.

Preparation of 3-(Anilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane by the Replacement of Chlorine by Anilino

A mixture of 40.5 g (0.15 mole) of 3-(chloromethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane and 41.8 g (0.45 mole) of aniline was prepared in a flask fitted with stirrer, thermometer, and condenser protected with a calcium chloride tube. The reaction mixture was stirred for six hours at 110°. The precipitate was filtered off, and vacuum fractionation of the filtrate gave 8 g (16.3%) of a product having b. p. 159-161° (22 cm), $n^{20}D$ 1.4651, d^{20}_4 0.952, yield 16.3%.

Found %: C 50.5, 50.9; H 8.69, 8.61; Si 24.67, 24.87; N 5.0, 5.1. $C_{14}H_{29}Si_3O_2N$. Calculated %: C 51.38; H 8.87; Si 25.65; N 4.3.

Found M 327, 319; Calculated M 327.

Preparation of α,α,α,ω,ω,ω-Hexamethylpoly[(N-ethylanilinomethyl)methyl]-Polysiloxanes $(CH_3)_3SiO[SiCH_3(CH_2NC_2H_5C_6H_5)O]_nSi(CH_3)_3$

By the cohydrolysis of 35.3 g (0.3 mole) of ethoxytrimethylsilane with 37.8 g (0.145 mole) of diethoxy(N-ethylanilinomethyl)methylsilane by means of 1.0 N NaOH under the conditions described for the first experiment we obtained 8.7 g of 3-(N-ethylanilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane, b. p. 141-144° (4 mm), $n^{20}D$ 1.4743, d^{20}_4 0.9416.

Found %: C 55.1, 53.0; H 9.9, 9.1; Si 23.4, 22.95; N 4.28, 4.26. $C_{16}H_{33}Si_3O_2N$. Calculated %: C 54.0; H 9.29; Si 23.6; N 3.95.

Found M 322; Calculated M 355.

The still residues from three experiments were combined and fractionated. We obtained 9.5 g of a product of b. p. 230-235° (3 mm), $n^{20}D$ 1.5065, d^{20}_4 1.015, which was found to be 3,5-bis(N-ethylanilinomethyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane,

Found %: C 56.13, 56.57; H 8.85, 8.69; Si 19.9, 19.7; N 6.0. $C_{26}H_{48}Si_4O_3N_2$. Calculated %: C 56.9; H 8.7; Si 20.4; N 5.1.

Found M 550; Calculated M 548.

and 11 g of a product of b. p. 278-284° (1 mm), n^{20}_4 1.5487, d^{20}_4 1.083, which was found to be 3,5,7-tris(N-ethylanilinomethyl)-1,1,1,3,5,7,9,9,9-nonamethylpentasiloxane.

Found %: C 59.1, 59.1; H 7.75, 7.5; Si 18.8, 18.4; N 6.6. $C_{36}H_{65}Si_5O_4N_3$. Calculated %: C 58.3; H 8.5; Si 18.9; N 5.67.

Found M 738; Calculated M 741.

Preparation of α,α,α,ω,ω,ω-Hexamethylpoly[(diethylaminomethyl)methyl]Polysiloxanes $(CH_3)_3SiO[SiCH_3CH_2N(C_2H_5)_2O]_nSi(CH_3)_3$

In the cohydrolysis of 37.8 g (0.15 mole) of (diethylaminomethyl)diethoxymethylsilane with 32.5 g (0.27 mole) of ethoxytrimethylsilane under the above-described conditions fractionation gave:

1) 6.3 g of 3-(diethylaminomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane, b. p. 68-71° (3 mm), $n^{20}D$ 1.4128, d^{20}_4 0.8560.

Found %: C 46.29, 46.74; H 10.97, 10.41; Si 27.52, 27.51; N 4.71, 4.61. $C_{12}H_{33}Si_3O_2N$. Calculated %: C 46.9; H 10.7; Si 27.36; N 4.5.

Found M 296; Calculated M 307.

2) 3.5 g of 3,5-bisdiethylaminomethyl-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, b. p. 115-130° (3 mm), $n^{20}D$ 1.4205, d^{20}_4 0.8909.

Found %: C 45.25, 45.14; H 10.76, 10.06; Si 24.6; N 6.46, 6.53. $C_{18}H_{48}Si_4O_3N_2$. Calculated %: C 47.8; H 10.6; Si 24.78; N 6.19.

Found M 454; Calculated M 452.

3) 3 g of 3,5,7,9-tetrakisdiethylaminomethyl-1,1,1,3,5,7,9,11,11,11-decamethylhexasiloxane, b. p. 205 to 215° (1 mm), $n^{20}D$ 1.4390, d^{20}_4 0.9659.

Found %: C 43.97, 43.55; H 9.58, 9.64; Si 24.0; N 8.81, 8.4. $C_{30}H_{78}Si_6O_5N_4$. Calculated %: C 48.5; H 10.52; Si 22.64; N 7.54.

Found M 780; Calculated M 742.

Preparation of α,α,α,ω,ω,ω-Hexamethylpoly[(o-chloroanilinomethyl)methyl] Polysiloxanes

In the cohydrolysis of 27.5 g (0.1 mole) of (o-chloroanilinomethyl)diethoxymethylsilane with 25.2 g (0.21 mole) of ethoxytrimethylsilane by means of 0.1 N NaOH under the above-described conditions, fractional distillation gave:

1) 6 g of 3-(o-chloroanilinomethyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane, b. p. 147-150° (3 mm), $n^{20}D$ 1.4752, d^{20}_4 1.002.

Found %: C 46.43, 46.29; H 8.00, 8.3; Si 22.73, 22.87; N 4.25; Cl 9.94, 10.1. $C_{14}H_{28}Si_3NClO_2$. Calculated %: C 46.47; H 7.75; Si 23.24; N 3.87; Cl 9.8.

Found M 340; Calculated M 261.5.

2) 2.8 g of 3,5-bis(o-chloroanilinomethyl)-1,1,1,3,5,7,7,7-octamethyltetrasiloxane, b. p. 208-215° (1 mm), $n^{20}D$ 1.513, d^{20}_4 1.097.

Found %: C 48.07, 48.40; H 6.68, 6.88; Si 19.07, 19.04; N 5.12, 5.0; Cl 12.2, 12.4. $C_{22}H_{38}Si_4O_3N_2Cl_2$. Calculated %: C 47.06; H 6.78; Si 19.96; N 4.99; Cl 12.63.

Preparation of 1,3-Bis(o-chloroanilinomethyl)-1,1,3,3-tetramethyldisiloxane

(o-Chloroanilinomethyl)ethoxydimethylsilane (6 g) was dissolved in 10 ml of ether, and 25 ml of 0.5 N NaOH was added. The mixture was stirred for four hours at 30-35°. The aqueous layer was separated, and the ether layer was washed with water until the reaction for OH^- was negative, dried over alkali, and vacuum-fractionated. The product (2.5 g) had b. p. 222-224° (5 mm), $n^{20}D$ 1.5425, d^{20}_4 1.1265.

Found %: C 51.6; H 5.4; Si 12.5; Cl 18.1; N 7.0, 7.1. $C_{18}H_{28}Si_2ON_2Cl_2$. Calculated %: C 52.3; H 6.3; Si 13.5; Cl 17.2; N 6.78.

Found M 450; Calculated M 413.

SUMMARY

1. By the cohydrolysis of ethoxytrimethylsilane with N-substituted (aminomethyl)diethoxymethylsilanes, liquid organosilicon polymers were obtained in which the terminal groups were trimethylsiloxy groups and there were 1, 2, and 3 intermediate organosilicon repeating units.

2. Activation energies for viscous flow were determined, and it was shown that, for a given degree of polymerization, the activation energy depends on the structure of the group introduced into the amino group. The investigated groups can be placed in the following order of diminishing activation energy for viscous flow: $ClC_6H_4NH > C_6H_5NH \geq C_6H_5C_2H_5N > (C_2H_5)_2N$.

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REACTION OF ETHYL BROMIDE WITH SILICON

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The present work was carried out with the object of studying the possibility of preparing alkylbromosilanes containing various organic groups [1]. As we have already noted [2], the direct reactions of propyl and butyl bromides with silicon give only very small yields of bromopropyl- and bromobutyl-silanes because of the almost complete pyrolysis of the original bromo compounds into hydrogen bromide and unsaturated hydrocarbons at temperatures below that necessary for the formation of the bromosilanes.

The reaction of ethyl bromide with silicon proceeds by schemes analogous to those for the formation of bromomethylsilanes [3, 4]. However, in the synthesis of bromoethylsilanes pyrolysis of ethyl bromide into ethylene and hydrogen bromide proceeds to a greater extent than the pyrolysis of methyl bromide in the synthesis of bromomethylsilanes and has an appreciable effect on the composition of the reaction products.

EXPERIMENTAL

The apparatus in which the reaction between ethyl bromide and silicon was carried out was an electrically heated tube furnace, 0.8 m in length; a glass tube, 1.2 m in length and 15 mm in diameter, was placed in the furnace. The tube was loaded with an intimate mixture of 60 g of silicon and 15 g of reduced copper. The silicon was first ground to a fine powder. Before the passage of the halogen compound through the tube, nitrogen was passed, and the furnace was heated to the temperature of the experiment. When the required temperature was reached, ethyl bromide was passed through the reaction tube in a stream of nitrogen. The reaction products were condensed in a receiver fitted with reflux condenser attached to a train of two receivers cooled to −70°.

We studied the reaction of ethyl bromide with silicon in the range 260-380°. The weight of reaction products was determined, and unchanged ethyl bromide was then distilled from the crude mixture. At 260-280° only 8-15% of the ethyl bromide reacted. With rise in temperature there was a sharp increase in the yields of the products of the reaction and of the pyrolysis of ethyl bromide (Table 1 and Fig. 1). Thus, at 380° 83% of the ethyl bromide reacted, and of this about 50% was used in the formation of silicon compounds, while the remainder underwent pyrolysis (Table 1).

The study of the composition of the products of the reaction of ethyl bromide with silicon was found to be extremely difficult, because the bromoethylsilanes, tetrabromosilane, and tetraethylsilane have very close boiling points: the boiling point of tetraethylsilane is 151°, that of tetrabromosilane is 153°, and those of the bromoethylsilanes range from 151 to 153°. Table 2 gives the fractional composition of products of the reaction of ethyl bromide with silicon.

The 110-125° fractions consisted of technical tribromosilane. In the 125-145° fractions we found considerable amounts of dibromoethylsilane (analysis for active hydrogen), the yield of which increased with rise in the temperature of reaction. By the reaction of the 125-145° fraction with cyclohexene we obtained dibromocyclohexylethylsilane [5]. To determine the composition of reaction products boiling above 145°, the 145-160° fractions were treated with butyllithium, the relative amounts of bromoethylsilanes being estimated from the amounts of butylethylsilanes isolated (these differ greatly in boiling point).

The treatment of 145-160° fractions obtained at 280°, 320°, 340°, and 380° with butyllithium was carried out in a three-necked flask fitted with stirrer, dropping funnel, reflux condenser, and inlet tube, through which

nitrogen was passed during the whole of the experiment. A mixture of butyl bromide and ether was added from the dropping funnel, with stirring, to finely cut lithium, a 1:1 mixture of the investigated fraction of bromo compounds with ether was added, and the reaction mixture was then heated in a water bath. The ethereal solution of organosilicon compounds was poured in small portions onto ground ice; the organic layer was then separated and dried with calcium chloride. Ether was distilled off, and then the n-octane, which was formed in our experiments as a by-product (obtained in 20-25% yield on the butyl bromide taken). The residue, which consisted of organosilicon compounds (silahydrocarbons), was fractionated to determine its quantitative composition.

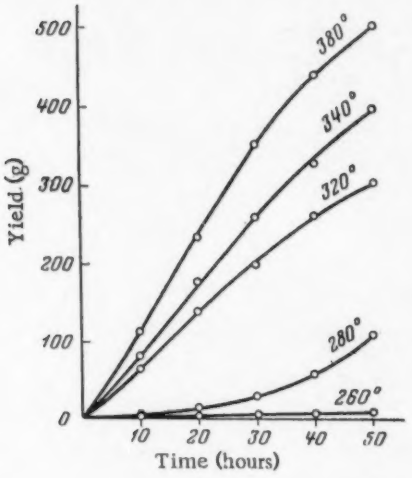

Fig. 1

1. The reactants were the fraction of b. p. 145-160° obtained at 280° (75 g), lithium (24 g), and ethyl bromide (240 g), and 53.5 g of organosilicon compounds was obtained. Table 3 gives the results of the fractionation of the reaction products. Fractions II and III were mixtures of small amounts of butyltriethyl- and dibutyldiethyl-silanes; Fraction IV was tributylethylsilane; Fraction V was tetrabutylsilane together with a little tributylethylsilane; and Fraction VI was tetrabutylsilane.

2. The reactants were the 145-160° fraction obtained at 320° (100 g), lithium (32 g), and butyl bromide (320 g), and 68 g of organosilicon compounds was obtained and was vacuum-fractionated through a column (Table 4).

Fraction I was a mixture of butyltriethyl- and dibutyldiethyl-silanes with a little n-octane; Fractions II and III consisted of tributylethylsilane. The residue contained a small amount of tributylethylsilane, tetrabutylsilane, and some condensation products.

TABLE 1

Amount (g) of	Temperature of experiment (° C)				
	260	280	320	340	380
Ethyl bromide recovered	915	850	585	452	172
Ethyl bromide that reacted	85	150	415	548	828
Reaction product	9.2	110	306	399	506

TABLE 2

Amt. of ethyl bromide passed (g)	Temp. of expt. (° C)	Amt. reaction products after removal of CH_3CH_2Br	Yield (g) of fraction of b. p.			
			110–125°	125–145°	145–160°	Residue
1000	260	9,2	—	—	—	—
1000	280	110	7,6	15	75	8,2
1000	320	306	10,8	47,9	223	22,3
1000	340	399	10,8	75,4	281,8	23,8
1000	380	506	12,1	79,0	385,3	24

3. The reactants were the 145-160° fraction obtained at 340° (100 g), lithium (32 g), and butyl bromide (320 g), and 78 g of organosilicon compounds was obtained and was vacuum-fractionated through a column (Table 5).

Fraction I was a mixture of n-octane, butyltriethylsilane, and dibutyldiethylsilane; Fractions II and III consisted of tributylethylsilane. The residue contained small amounts of tributylethylsilane and tetrabutylsilane.

TABLE 3

Fraction	B. p. (° C)	Amount (%)	$n^{20}D$
I	200—214	2,2	
II	214—220	6,6	1,4392
III	220—227	9,9	1,4423
IV	230—235	23,4	1,4440
V	235—256	16,8	1,4458
VI	256—258	34,0	1,4462
VII	258—270	5,6	
Losses		1,5	

TABLE 4

Fraction	B. p. in ° C (p in mm)	Amt. (%)	n_D^{20}
I	60—108 (5)	12,3	1,4312
II	108—110 (5)	17,4	1,4440
III	110—116 (5)	33,3	1,4438
Residue		33,8	
Losses		3,2	

TABLE 5

Fraction	B. p. in ° C (p in mm)	Amt. (%)	n_D^{20}
I	45—95 (2)	20,2	1,4215
II	95—97 (2)	4,6	1,4439
III	97—100 (2)	46,6	0,4440
IV	100—110 (2)	1,5	
Residue		24,0	
Losses		3,4	

TABLE 6

Fraction	B. p. in ° C (p in mm)	Amt. (%)	n_D^{20}
I	50—93 (2)	13,5	1,4440
II	93—95 (2)	26,0	1,4440
III	95—96 (2)	25,0	1,4440
IV	96—98 (2)	12,4	
V	98—115 (2)	6,2	
Residue		15,6	
Losses		1,3	

4. The reactants were the 145-160° fraction obtained at 380° (200 g), lithium (64 g), and butyl bromide (640 g), and 151 g of organosilicon compounds was obtained and was vacuum-fractionated through a column (Table 6).

Fraction I was a mixture of dibutyldiethylsilane, butyltriethylsilane, and n-octane; Fractions II-IV consisted of tributylethylsilane; Fraction V was a mixture of tributylethylsilane and tetrabutylsilane. The residue contained tetrabutylsilane and condensation products.

On the basis of the analyses of 145-160° fractions and the results of the organolithium syntheses it may be concluded that with rise in temperature in the reaction between ethyl bromide and silicon the yield of tribromoethylsilane rises sharply. At 320-380° tribromoethylsilane is the main reaction product (Table 7, Fig. 2).

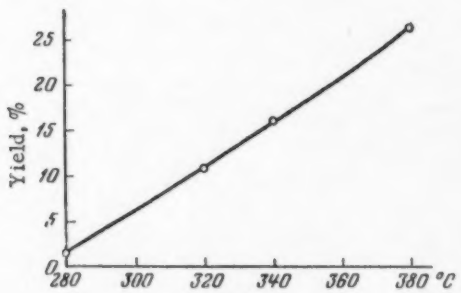

Fig. 2

The 145-160° fractions contained also small amounts of bromotriethyldibromodiethyl-, and tetrabromosilanes. With rise in reaction temperature the yield of dibromodiethylsilane fell.

TABLE 7

Yield of tribromo-ethylsilane (%)	Reaction temperature (°C)			
	280	320	340	380
On amount of ethyl bromide passed (1000 g)	1.6	10.9	16.1	26.4
On the ethyl bromide that reacted	9.4	24.1	28.4	32.4
Content of tribromo-silane (% on total amount of silicon compounds)	11.2	32.9	34.8	48.0

We list below the silahydrocarbons that we isolated as a result of treatment of the 145-160° fractions with butyllithium.

Dibutyldiethylsilane: B. p. 68-70° (2 mm); d^{20}_4 0.7882; $n^{20}D$ 1.4400; found MR 66.82; calculated MR 67.82.

Found %: C 72.47, 72.57; H 13.78, 13.83. Calculated %: C 71.91; H 14.08.

Tributylethylsilane: B. p. 95-96° (2 mm); d^{20}_4 0.7913; $n^{20}D$ 1.4440; found MR 76.64; calculated MR 76.58.

Found %: C 73.61, 73.69; H 14.65, 14.62. Calculated %: C 73.68; H 14.03.

Tetrabutylsilane: B. p. 120-121° (2 mm); d^{20}_4 0.7971; $n^{20}D$ 1.4466; found MR 85.72; calculated MR 85.84.

Found %: C 74.85, 74.78; H 14.43, 14.45. Calculated %: C 74.89; H 14.17.

SUMMARY

1. The reaction of ethyl bromide with silicon in presence of reduced copper was studied in the temperature range 260-380°.

2. The main reaction product was tribromoethylsilane, the yield of which increased considerably with rise in reaction temperature. As a result of the partial pyrolysis of ethyl bromide at the temperature of the formation of bromoethylsilanes, the formation of dibromodiethylsilane, and particularly of bromotriethylsilane, occurred to a much lower extent. The reaction products included also silicon compounds containing silicon-attached hydrogen, namely tribromo- and dibromoethyl-silanes.

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SYNTHESIS OF NEW KINDS OF SILICON-CONTAINING MONOMERS

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In the last decade there have been numerous investigations devoted to new problems in the synthesis of organosilicon compounds: 1) methods of introducing various functional groups into the hydrocarbon groups of alkylchlorosilanes (introduction of double bonds, halogens, and groups such as cyano, butadienyl, and carboxyl); 2) the discovery of polymerizable silahydrocarbons and their derivatives; 3) methods of preparing compounds in which metals and other elements (Al, Ti, B, etc.) are introduced into the siloxane chain. These methods and the substances prepared by them are discussed in our review articles [1], in a review by George, Prober, and Elliot [2], and in papers by Andrianov [3]. In the present paper we shall discuss mainly material from investigations that have not yet been published, and we shall classify this as follows: 1) catalytic addition of silanes containing silicon-attached hydrogen to unsaturated and aromatic compounds; 2) high-temperature condensation of silanes containing silicon-attached hydrogen with alkyl, aryl, and alkenyl halides; 3) synthesis of polymerizable silahydrocarbons and their derivatives.

Catalytic Addition of Silanes Containing Silicon-Attached Hydrogen to Unsaturated and Aromatic Compounds

Work of American investigators [4] showed that the highest yields in the addition of silanes to substances containing a multiple bond in presence of peroxides are given by compounds of the type $HSiX_3$ (X = halogen). We found that in presence of catalysts (platinized charcoal, ruthenium on alumina, which was used by us for the first time, and others) silanes of the types $RSiHCl_2$ and R_2SiHCl give higher yields than trichlorosilane. It was later shown that the highest yields of addition products are given by substances having an "active" double bond (butadiene, allyl and 2-methylallyl chlorides), whereas lower yields are obtained with compounds in which the double bond is "screened" by halogens (tetrafluoroethylene, chlorotrifluoroethylene). It was shown also that, whereas in the latter cases addition requires more severe conditions (high pressure, 160-180°, and platinized charcoal catalyst), in the simpler cases of these reactions it is possible, as Ponomarenko and Cherkaev [12] showed, to use extremely mild conditions: 20-60°, low or even atmospheric, pressure, and homogeneous conditions of reaction in presence of Speier's catalyst (solution of H_2PtCl_6 in isopropyl alcohol):

$$CH_3Cl_2SiH + CH_2 = CH_2 \rightarrow CH_3C_2H_5SiCl_2 \qquad (\sim 100\%)$$

$$CH_3Cl_2SiH + CH \equiv CH \rightarrow CH_3Cl_2SiCH = CH_2 \qquad (\sim 100\%)$$

$$(C_2H_5)_3SiH + CH_2 = CH - CH = CH_2 \rightarrow (C_2H_5)_3SiCH_2CH = CHCH_3 \qquad (50\%)$$

$$(C_2H_5)_3SiH + CH \equiv C - CH = CH_2 \rightarrow (C_2H_5)_3SiCH = CHCH = CH_2 \qquad (50\%)$$

In spite of the use of such mild conditions in the first two reactions, almost quantitative yields are obtained, which, considered in relation to the accessibility of dichloroalkylsilanes, is of practical interest. In the case of butadiene and 1-buten-3-yne the yields are lower as a result of side reactions (polymerization) of these hydrocarbons.

It was finally shown that in the catalytic addition of silanes containing silicon-attached hydrogen not only the yields, but also the direction of addition are determined by the structure of the unsaturated compound to which addition is occurring. In the case of allyl and 2-methylallyl chlorides the silicon-attached hydrogen adds to the less hydrogenated atom of the hydrocarbon, and the residue to the more hydrogenated atom. In the case of vinyl chloride addition is in the opposite direction. As Nesmeianov and Freidlina showed [5], addition of silanes containing silicon-attached hydrogen to unsaturated compounds can occur not only in presence, but also in absence of catalysts (under pressure). In this case addition is accompanied by telomerization.

In the further development of the investigation of the catalytic addition of silanes containing silicon-attached hydrogen to fluoro olefins we recently showed, in collaboration with Odabashian, that, unlike tetrafluoro- and chlorotrifluoro-ethylenes, fluorinated ethers (allyl tetrafluoroethyl and chlorotrifluoroethyl ethers) form addition products with silanes containing silicon-attached hydrogen in high yields. The resulting fluoro ethers, containing chlorosilyl groups, are shown in Table 1. Addition was carried out under constant conditions: 160-170°, 3 hours, 0.3 g of 1% Pt—C catalyst. It will be seen that in the case of unsaturated ethers the highest yields are given by silanes in which the number of chlorine atoms is 2 or 1; silanes containing three chlorine atoms follow, and the lowest yields of addition products are given by trialkylsilanes. For comparison purposes, in Table 1 we give also the yield of the product of the addition (under the same conditions) of dichloromethylsilane to $CF_2=CFCl$.

TABLE 1

Original silane	Addition product	Yield (%)
$HSiCl_3$	$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	38
CH_3Cl_2SiH	$CH_3Cl_2SiCH_2CH_2CH_2OCF_2CFClH$	76
$C_2H_5Cl_2SiH$	$C_2H_5Cl_2SiCH_2CH_2CH_2OCF_2CFClH$	76
n-$C_3H_7Cl_2SiH$	n-$C_3H_7Cl_2SiCH_2CH_2CH_2OCF_2CFClH$	61
$CH_3(C_2H_5)SiClH$	$CH_3(C_2H_5)ClSiCH_2CH_2CH_2OCF_2CFClH$	50
$CH_3(C_2H_5)_2SiH$	$CH_3(C_2H_5)SiCH_2CH_2CH_2OCF_2CFClH$	14
CH_3Cl_2SiH	$CH_3SiCl_2CFClCF_2H$	4,5

These ethers, containing fluorine and chlorosilyl groups, are fairly stable to heat; the fluoro ether grouping in these compounds is not affected in the course of Grignard reactions and in hydrolysis.

As Chernyshev showed [6], silanes containing silicon-attached hydrogen can condense also with aromatic hydrocarbons, though under more severe conditions (heating in an autoclave to 300°, Raney nickel or $AlCl_3$ catalyst). The following reactions have been carried out:

$$HSiCl_3 + C_6H_6 \rightarrow Cl_3SiC_6H_5 \quad (32\%)$$
$$CH_3Cl_2SiH + C_6H_6 \rightarrow CH_3Cl_2SiC_6H_5 \quad (23\%)$$
$$CH_3Cl_2SiH + C_6H_5CH_3 \rightarrow CH_3Cl_2SiC_6H_4CH_3 \quad 30\%)$$
$$CH_3Cl_2SiH + C_6H_5Cl \rightarrow CH_3Cl_2SiC_6H_4Cl \quad \text{traces}$$

Here, the one-stage synthesis of methylphenyl- and methyltolyl-dichlorosilanes is the most interesting feature.

High-Temperature Condensation of Silanes Containing Silicon-Attached Hydrogen With Alkyl, Aryl, and Alkenyl Halides

Reactions of this kind were first studied by Agre; we extended them to new pairs of compounds and, in particular, we were the first to study the condensation of the readily accessible dichloromethyl- and dichloroethyl-silanes with various alkenyl and aryl chlorides. The reactions were carried out in an empty glass tube heated to 550-600°. The reactions studied by Mironov [7] are given in Table 2, and those studied by Chernyshev and Li in Table 3.

It will be seen from Tables 2 and 3 that the high-temperature condensation reaction can be used for the synthesis of previously difficultly accessible compounds: some have not been prepared before, and some have been obtained only in very low yield.

Of the reactions cited, those with chlorotrifluoroethylene and chloronaphthalene are of special interest. By direct synthesis it has been possible to prepare trichloronaphthylsilane in yields of not more than 10%, even when silver was added to Si—Cu [8]. Higher yields were attained only by passage of a mixture of 1-chloronaphthalene and HCl at 540°, i.e., under conditions under which $HSiCl_3$ would evidently be formed in the first place. By the present method trichloronaphthylsilane can be obtained in 55% yield from chloronaphthalene and trichlorosilane in absence of catalysts. The one-stage synthesis of $CH_3Cl_2SiCF=CF_2$ from dichloromethylsilane and chlorotrifluoroethylene is of interest.

TABLE 2

Silane	Second reactant	Reaction product	Yield (%)
CH_3Cl_2SiH	$CH_2=CHCl$	$CH_3Cl_2SiCH=CH_2$	50
$C_2H_5Cl_2SiH$	$CH_2=CHCl$	$C_2H_5Cl_2SiCH=CH_2$	30
CH_3Cl_2SiH	$CH_2=CHCH_2Cl$	$CH_3Cl_2SiCH_2CH=CH_2$	30
CH_3Cl_2SiH	$(CH_3)_2C=CHCl$	$CH_3Cl_2SiCH=C(CH_3)_2$	20
CH_3Cl_2SiH	$ClCH=CHCl$	$CH_3Cl_2SiCH=CHCl$	20
CH_3Cl_2SiH	$ClCH=CCl_2$	$CH_3Cl_2SiCH=CCl_2$	27
CH_3Cl_2SiH	$CF_2=CFCl$	$CH_3Cl_2SiCF=CF_2$	30

TABLE 3

Silane	Second reactant	Reaction product	Yield (%)
Cl_3SiH	C_6H_5Cl	$Cl_3SiC_6H_5$	50
CH_3Cl_2SiH	C_6H_5Cl	$CH_3Cl_2SiC_6H_5$	40
Cl_3SiH	α-$ClC_{10}H_7$	$Cl_3Si\alpha$-$C_{10}H_7$	55
CH_3Cl_2SiH	α-$ClC_{10}H_7$	$CH_3Cl_2Si\alpha$-$C_{10}H_7$	30
$C_2H_5Cl_2SiH$	α-$ClC_{10}H_7$	$C_2H_5Cl_2Si\alpha$-$C_{10}H_7$	20
Cl_3SiH		$Cl_3Si\alpha$-$C_{10}H_7$ $Cl_3SiC_6H_4Cl$	20 10

Synthesis of Polymerizable Silahydrocarbons and Their Derivatives

Some years ago we synthesized various mono-, di-, and poly-alkenylsilanes in which the double bond was in the α-, β-, or γ-position with respect to silicon, and their polymerizability in presence of peroxides and other catalysts was investigated by Korshak and Poliakova [9]; they showed that solid macromolecular polymers were formed only by di- and poly-alkenylsilanes; in this case three-dimensional polymers were obtained which were of interest because of their high thermal stability. Monoalkenylsilanes give linear polymers, but they are oils and the degree of polymerization does not exceed 18. It was shown that this low polymerizability of monoalkenylsilanes is to be explained entirely by the structure of the original monomers, and not by the inhibiting effect of the silicon atom on the double bond, as assumed previously by some investigators. On the other hand, vinyl- and allyl-trimethylsilanes have higher polymerizability than their carbon analogs. As will be seen from the results given in the figure, the extent of radical-induced polymerization is the lower, the higher the rate of ionic addition reactions (the figure shows the rate of addition of thiocyanogen).

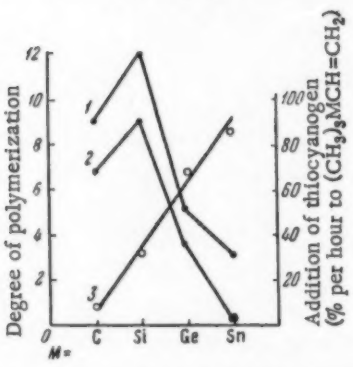


Fig. Degree of polymerization for : 1) $(CH_3)_3MCH=CH_2$; 2) $(CH_3)_3MCH_2CH=CH_2$; 3) rate of addition of thiocyanogen.

We reported recently that in the search for new forms of polymers we synthesized allyl-, 2-methylallyl-, allyloxy-, and also some

ethynyl-silanes containing silicon-attached hydrogen, and we carried out their polymerization into polymers containing a silicon atom in the main chain in accordance with the scheme:

$$H-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}CH_2CH=CH_2 \xrightarrow{Pt/C} \left(-\underset{R}{\overset{R}{\underset{|}{\overset{|}{Si}}}}CH_2CH_2-CH_2-\right)_n$$

It was later shown that in presence of peroxides this monomer also polymerizes in accordance with the usual scheme for alkenylsilanes:

$$HR_2SiCH_2CH=CH_2 \xrightarrow{peroxide} \left(-CH_2-\underset{HSiR_2}{\underset{|}{CH}}-\right)_n$$

(i.e., with silicon atoms in the side chains). It is interesting that the polymer obtained over Pt/C had a degree of polymerization of n = 25, whereas the polymer obtained in presence of peroxides had n = 9.

In view of the fact that macromolecular polymers are formed particularly readily from monomers having conjugated double bonds, e.g., butadiene, isoprene, acrylic esters, styrene, and also vinyl ethers and acetals, we decided to undertake the synthesis of silicon-containing derivatives of these compounds. First attempts to condense silanes containing silicon-attached hydrogen with butenyne were unsuccessful. Under the conditions used (Pt/C catalyst, 150-160°) the reaction went, but the resulting butadienylsilane immediately polymerized. Recently, by the use of H_2PtCl_6 at room temperature, we succeeded in preparing not only the above-mentioned butadienyltriethylsilane, but also the following monomers; yields were 40-50%:

$$CH_3Cl_2SiH + HC\equiv CCH=CH_2 \rightarrow CH_3Cl_2SiCH=CH-CH=CH_2,$$
$$Cl_3SiH + HC\equiv CCH=CH_2 \rightarrow Cl_3SiCH=CH-CH=CH_2.$$

The direction of addition was established by comparison of spectrum-analysis data for these compounds with those for compounds of the same structure prepared by Grignard synthesis.

As we expected in the butadienylsilane series, 2-methyl-3-(triethylsilyl)-1,3-butadiene, which is structurally similar to isoprene and was prepared by the reaction

$$(C_2H_5)_3SiH + CH\equiv \overset{OH}{\overset{|}{C}}(CH_3)_2 \xrightarrow[-H_2O]{Pt/C} CH_2=\underset{Si(C_2H_5)_3}{\underset{|}{C}}-C=CH_2,\ \ C-CH_3$$

gave a polymer of higher molecular weight than 1-(triethylsilyl)butadiene.

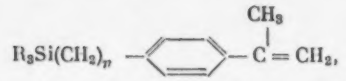
Acrylic acid derivatives were prepared according to the equations:

$$(CH_3)_3SiCH=CHMgBr + CO_2 \rightarrow (CH_3)_3SiCH=CHC\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$$

$$(CH_3)_3Si\underset{CH_2}{\underset{\|}{C}}MgBr + CO_2 \rightarrow (CH_3)_3Si\underset{CH_2}{\underset{\|}{C}}\cdot C\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$$

These silicon-containing substituted acrylic acids are solids of m. p. 50° and 25°; the polymerizability of them and their esters is being examined.

Chernyshev and Tolstikova have synthesized various silicon-containing styrenes and α-methylstyrenes, of the type:



in which n = 0, 1, and 2, by the Grignard reaction. It was found that in polymerization by the free-radical mechanism, unlike alkenylsilanes, they form solid glassy polymers, even without application of pressure. The resulting polymers had higher glass points than polystyrene. Thus, polymerized p-(triethylsilyl)styrene has a glass point of 100°, whereas that of polystyrene is 80-85°. Copolymers have still better properties: the copolymer of p-(triethylsilyl) styrene with styrene has a glass point of 120°.

These results prompted us to search for simple methods of synthesizing silicon-containing styrenes. In collaboration with workers from Balandin's laboratory we developed a catalytic method for the preparation of silicon-containing styrenes in 50-90% yield: dehydrogenation of ethylphenylsilanes over a copper-chromium catalyst. If we take silanes containing silicon-attached hydrogen and ethylbenzene as reactants, then the whole synthesis of the silicon-containing styrenes can be carried out in two stages:

$$CH_3Cl_2SiH + C_6H_5C_2H_5 \xrightarrow{AlCl_3} CH_3Cl_2SiC_6H_4C_2H_5 + H_2,$$

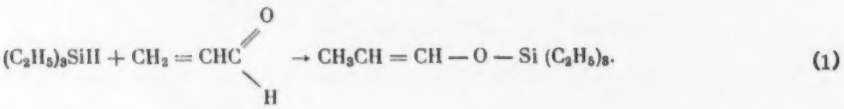
$$CH_3Cl_2SiC_6H_5C_2H_5 \xrightarrow{Cu-Cr} CH_3Cl_2SiC_6H_4CH = CH_2.$$

Silicon-Containing Vinyl Ethers and Acetals

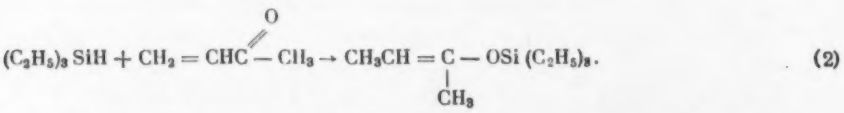
As is well known, vinyl ethers are synthesized by the simple Favorskii reaction:

$$CH \equiv CH + ROH \xrightarrow{KOH} CH_2 = CHOR,$$

which is not applicable, however, to silanols. Silicon-containing vinyl ethers have been prepared by a reaction first observed by us: by 1,4-addition of a trialkylsilane to an α, β-unsaturated aldehyde or ketone:

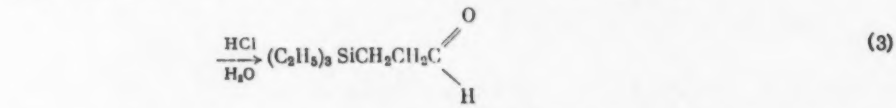


(1)



(2)

To prove that addition is in the 1,4-positions, and not in the 1,2-positions with formation of 3-(triethylsilyl) propionaldehyde, this aldehyde was synthesized as follows:



(3)

The compound prepared by reaction (1) had b. p. 49-50° (6 mm), $n^{20}D$ 1.4320, d^{20}_4 0.8363; it was readily hydrolyzed by boiling dilute sulfuric acid with formation of propionaldehyde (m. p. of 2,4-dinitrophenylhydrazone 155°). The compound prepared by reaction (3) had b. p. 77-78° (5 mm), $n^{20}D$ 1.4472, d^{20}_4 0.8692, and when boiled with dilute sulfuric acid it did not break down at the Si–C bond; 2,4-dinitrophenylhydrazine gave a hydrazone of m. p. 105° which corresponded in analysis to the hydrazone of 3-(triethylsilyl)propionaldehyde. It was shown that dichloroethylsilane adds to acrolein in the same way as triethylsilane:

$$C_2H_5Cl_2SiH + CH_2 = CHC(=O)H \rightarrow CH_3CH = CHOSi(C_2H_5)Cl_2.$$

Dichloroethyl(propenyloxy)silane polymerizes spontaneously to a thick oil, which is converted to hydrolysis into a solid silicone. The hydrolysis of silicon-containing vinyl ethers

$$CH_3CH = CHOSi(C_2H_5)_3 \xrightarrow{H_2O} (C_2H_5)_3SiOH + CH_3CH_2C(=O)H$$

not only proves the structures of the ethers, but can serve as a convenient method of reducing α, β-unsaturated aldehydes (ketones) to the saturated compounds.

Another type of vinyl ether was prepared by the reaction:

$$CH_3Cl_2SiH + HC \equiv COR \rightarrow CH_3Cl_2SiCH = CHOR.$$

By addition of triethylsilane to an acrylic ester, also in presence of H_2PtCl_6, an acetal of the olefin series was obtained:

$$(C_2H_5)_3SiH + CH_2 = CHC(=O)OCH_3 \rightarrow (C_2H_5)_3SiOC(=CHCH_3)OCH_3,$$

its structure (i.e., that addition is again in the 1,4-positions) was proved by the condensation of triethylsilane with acrylic acid

$$(C_2H_5)_3SiH + CH_2 = CHC(=O)OH \rightarrow [(C_2H_5)_3SiOC(OH) = CHCH_3] \rightarrow (C_2H_5)_3SiOC(=O)C_2H_5,$$

as a result of which triethylsilyl propionate was obtained; this was recently synthesized by Andreev and Dolgov [10] by another reaction (action of chlorotriethylsilane on potassium propionate). The properties of the two products were found to be identical.

It is of interest that, as Speier showed [11], over platinized charcoal at 160° the addition of CH_3SiCl_2H to an acrylic ester proceeds in a different way:

$$CH_3Cl_2SiH + CH_2 = CHC(=O)OCH_3 \xrightarrow{Pt/C} CH_3Cl_2SiCH_2CH_2C(=O)OCH_3$$

Here addition is in the 1,2-positions and the product is methyl 3-(dichloromethylsilyl) propionate.

Under our conditions, under reflux in presence of H_2PtCl_6, addition went according to the scheme:

$$CH_3Cl_2SiH + CH_2 = CHC(=O)OCH_3 \rightarrow \begin{cases} CH_3Cl_2SiOC(OCH_3)=CHCH_3 & (10\%) \\ CH_3Cl_2SiCH_2CH_2C(=O)OCH_3 & (4\%) \\ CH_3Cl_2SiCHC(=O)OCH_3 \,(CH_3) & (17{,}5\%) \end{cases}$$

i.e., in the 1,4-positions to the extent of 10 % and in the 1,2-positions to the extent of 22%. The investigation of the polymerization of silicon-containing vinyl ethers has only just begun. From preliminary observations by Kolesnikov it appears that they polymerize in presence of $TiCl_4$ at 30-50° or in presence of triisobutylborine $(i\text{-}C_4H_9)_3B$ at 50°. In both cases solid linear polymers are formed.

In conclusion, I should like to express my great satisfaction with the fact that we carried out the synthesis of the monomers in close collaboration with scientists working on their polymerization at the All-Union Synthetic Rubber Research Institute and in Project No. 4019 and, in particular, in collaboration with Poliakova in Korshak's laboratory.

EXPERIMENTAL

1. Addition of CH_3SiHCl_2 to $CH_2=CF_2$ in Presence of Chloroplatinic Acid.* A 500 ml autoclave was charged with 124 g of CH_3SiHCl_2 and 0.25 ml of a 0.5 M solution of $H_2PtCl_6 \cdot 6H_2O$ in $i\text{-}C_3H_7OH$; the agitated mixture was saturated with $CH_2=CF_2$. The initial pressure was 17 atm. The autoclave was heated rapidly to 160° and maintained at this temperature for two hours. In the course of this time the pressure in the autoclave fell from 35 to 6 atm and then began to rise slowly. The autoclave was cooled and unloaded, and 150 g of a mixture of reaction products was obtained; fractionation of this through a column of 35-plate efficiency gave:

1) 10 g of CH_3SiCl_2F, b. p. 28.8-29.6° (740.7 mm);

Found %: C 51.75; F 14.82. CH_3SiCl_2F. Calculated %: C 53.32; F 14.29.

(the literature [7] gives b. p. 29.5° (760 mm));

2) 27.5 g of unchanged CH_3SiHCl_2, b. p. 40.9° (743.5 mm);

3) 61 g (34%) of $CH_3Si(Cl)_2CH_2CF_2H$, b. p. 113-113.2° (743.5 mm); d^{20}_4 1.2790; $n^{20}D$ 1.3991; found MR 34.06; calculated MR 34.23.

Found %: C 20.60, 20.52; H 3.30, 3.28; Cl 39.59, 39.18; F 21.67, 21.54. $CH_3Si(Cl)_2CH_2CF_2H$. Calculated %: C 20.12; H 3.38; Cl 39.55; F 21.22.

4) 18 g of high-boiling products.

2. Addition of CH_3SiHCl_2 to $CH_2=CH_2$.* Ethylene at 15 atm was passed from a cylinder into a 500 ml autoclave containing 115 g of CH_3SiHCl_2 and 0.25 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ solution. On agitation the pressure fell and the temperature of the autoclave rose spontaneously to 35°. In 30 minutes about one molecular proportion of ethylene was absorbed. The weight of reaction product was 138 g. In its fractionation through a column only $CH_3Si(Cl_2)CH_2CH_3$ (117 g) was isolated; b. p. 100° (743 mm). The yield of pure $CH_3Cl_2SiC_2H_5$ was 83%.

3. Addition of CH_3SiHCl_2 to $HC \equiv CH$.* Acetylene at 19 atm was passed into a 500 ml autoclave containing 64 g of CH_3SiHCl_2 and 1.2 ml of a 0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in $i\text{-}C_3H_7OH$. The autoclave was agitated, and in the first two hours the pressure fell to 9 atm and the temperature in the autoclave rose to 25°. Several further additions of acetylene were made. The pressure in the autoclave fell overnight to 8 atm. In all, about 0.6 of a molecular proportion of acetylene was absorbed in 21 hours. The product amounted to 73 g fractionation of which through a column gave only $CH_3Cl_2SiCH=CH_2$ (63 g), b. p. 92.5° (743.2 mm); yield of pure $CH_3Cl_2SiCH=CH_2$ was 81%.

4. 2-Chloro-1,1,2-trifluoroethyl 3-(Dichloromethylsilyl) propyl Ether $CH_3Cl_2SiCH_2CH_2CH_2OCF_2CFClH$**. A mixture of 60 g (0.52 mole) of dichloromethylsilane and 92 g (0.53 mole) of $CH_2=CHCH_2OCF_2CFClH$ was heated at 170° in presence of 0.3 g of 1% Pt on charcoal for three hours. The maximum pressure was 10 atm. The weight of reaction products was 147 g; fractionation through a column with aglass filling gave 115 g (76%) of pure $CH_3Cl_2SiCH_2CH_2CH_2OCF_2CFClH$; b. p. 215° (753 mm); d^{20}_4 1.3395, $n^{20}D$ 1.4160; found MR 54.26; calculated MR 54.76.

* These experiments were carried out in collaboration with Cherkaev and Zadorozhnyi [12].

** Experiments 4 and 5 were carried out by us in collaboration with Odabashian.

Found %: C 25.33, 25.37; H 3.62, 3.61; Cl 36.49; F 19.68, 19.70. $C_6H_{10}SiCl_3F_3O$. Calculated %: C 24.89; H 3.48; Cl 36.72; F 19.68.

5. 3-(Dichloroethylsilyl)propyl-1,1,2,2-Tetrafluoroethyl Ether. $C_2H_5Cl_2SiCH_2CH_2CH_2OCF_2CF_2H$. This was prepared under the conditions of Experiment 4 from $C_2H_5SiCl_2H$ and $CH_2=CHCH_2O-CF_2CF_2H$;* b. p. 75-78° (19 mm); d^{20}_4 1.2648, $n^{20}D$ 1.3955; found MR 54.49; calculated MR 54.38.

6. 2-(Trimethylsilyl) acrylic Acid.* A Grignard reagent was prepared from 5 g of magnesium and 38 g of (1-bromovinyl) trimethylsilane in 150 ml of tetrahydrofuran, and the product was poured onto 500 g of crushed solid carbon dioxide. On the next day the contents of the beaker were treated with water and 10% H_2SO_4. The aqueous layer was extracted with ether. Ether and tetrahydrofuran were distilled off, and vacuum distillation of the liquid residue gave 18 g of a fraction of b. p. 97-105° (13 mm), which rapidly solidified. After redistillation the substance came over at 100-101° (13 mm) and solidified immediately. After being washed with benzene, 2-(trimethylsilyl) acrylic acid had m. p. 50°; yield 64%. The acid equivalent, determined by titration with 0.1 N alkali, corresponded to the calculated value.

Found %: C 50.28, 50.20; H 8.47, 8.46; Si 19.01, 19.31. $C_6H_{12}SiO_2$. Calculated %: C 50.00; H 8.33; Si 19.44.

Similarly, from (2-bromovinyl) trimethylsilane we obtained 3-(trimethylsilyl) acrylic acid; yield 46%; $n^{25}D$ 1.4500, m.p. 15.5°; b. p. 113° (13 mm).

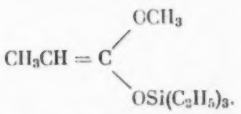
7. Allyldichloromethylsilane $CH_3Cl_2SiCH_2CH=CH_2$. A mixture of 400 g of dichloromethylsilane and 220 g of allyl chloride was passed at the rate of one drop per second through an empty glass tube heated to 600°. Fractionation of the condensate through a column gave 90 g of allyldichloromethylsilane; b. p. 120-121°; $n^{20}D$ 1.4419, d^{20}_4 1.0780; found MR 38.50; calculated MR 38.45.

8. 2-(Dichloromethylsilyl)vinyl Isopropyl Ether $CH_3Cl_2SiCH=CHOC(CH_3)_2$. To a mixture of 12 g of ethynyl isopropyl ether and 16.2 g of dichloromethylsilane, 1 ml of a 0.1 M solution of chloroplatinic acid in isopropyl alcohol was added. The mixture was heated to 145° for 12 hours. Vacuum distillation gave 6.5 g (21%) of 2-(dichloromethylsilyl)vinyl isopropyl ether; b. p. 48° (7 mm); $n^{20}D$ 1.4440, d^{20}_4 1.0710, found MR 49.39; calculated MR 49.32; yield 21%.

Found %: Si 14.25, 14.20; Cl 35.60, 35.50. $C_6H_{12}OCl_2Si$. Calculated %: Si 14.15; Cl 35.60.

9. Triethylpropenylsilane $CH_3CH=CHOSi(C_2H_5)_3$. A mixture of 112 g of freshly distilled acrolein and 0.5 ml of a 0.1 M solution of chloroplatinic acid in isopropyl alcohol was prepared in a one-liter flask fitted with stirrer and a reflux condenser protected by a calcium chloride tube. With continuous stirring 20 g of $(C_2H_5)_3SiH$ of the total calculated amount of 174 g was added. The temperature rose spontaneously to 35°. The reaction mixture was warmed in a water bath to 50-60°, and the temperature in the flask then rose rapidly to 110°, so that it was necessary to apply cooling. The further addition of triethylsilane was carried out dropwise, and the rate of addition was controlled so that the temperature was maintained at 45-50°. The reaction was completed by heating the mixture for one hour at 140-160°. Unchanged acrolein and triethylsilane were distilled off under atmospheric pressure. The residue (230 g) was fractionated at a residual pressure of 6 mm. This gave 160 g of triethylpropenylsilane, b. p. 49-50° (6 mm).

10. 1-Methoxy-1-(triethylsiloxy) propene



A mixture of 58 g of triethylsilane and 0.3 ml of a 0.1 M solution of H_2PtCl_6 in isopropyl alcohol was prepared in a flask fitted with reflux condenser and stirrer. The mixture was stirred for 30 minutes while 39 g of freshly distilled methyl acrylate was added. The temperature of the reaction mixture rose spontaneously to 76°. The reaction was completed by heating the mixture to 160°. The reaction product (96 g) was fractionated at a residual pressure of 5 mm. The yield of acetal, b. p. 70° (5 mm), was 80 g.

* Experiments 6-8 were carried out by Mironov in collaboration with Nepomnina and Maksimova.

SUMMARY

1. In presence of H_2PtCl_6 addition of alkyldichlorosilanes to $CH \equiv CH$, $CH_2=CH_2$, and $CH_2=CHCH_3$ proceeds in almost quantitative yield at 20-60°.

2. In presence of platinum catalysts alkyldichlorosilanes give the higher yields of addition products, whereas in presence of peroxides, trichlorosilane gives the higher yields.

3. By the condensation of alkyldichlorosilanes and trichlorosilane with aryl and alkenyl halides at 600°, previously inaccessible di- and tri-chlorosilanes were prepared.

4. Silicon-containing derivatives of butadiene, acrylic acids, and vinyl ethers and acetals were synthesized for the first time; these compounds give solid linear polymers at atmospheric pressure.

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SYNTHESIS OF OCTAALKYLPYROPHOSPHORAMIDES AND OCTAALKYLTHIOPYROPHOSPHORAMIDES

K. V. Nikonorov and Z. G. Speranskaia

Pyrophosphoric and thiopyrophosphoric esters, e.g. tetraethyl pyrophosphate, tetraethyl thiopyrophosphate, and tetraethyl dithiopyrophosphate, are powerful contact insecticides [1]. Nitrogen-containing derivatives of pyrophosphoric acid, e.g., octamethylpyrophosphoramide, are used as insecticides which function as stomach poisons [2]. The study of new members of this class of compounds may have not only theoretical, but also practical interest. In the present investigation we have prepared some alkylamides of pyrophosphoric and thiopyrophosphoric acids and have tested their insecticidal properties.

Octaalkylpyrophosphoramides and octaalkylthiopyrophosphoramides were prepared by heating the tetraalkylphosphorodiamidic chloride and the tetraalkylphosphorodiamidothioic chloride, respectively, with the ethyl tetraalkylphosphorodiamidate [3]. Octaethylpyrophosphoramide and symmetrical tetraethyltetramethylpyrophosphoramide were prepared by the hydrolysis of the tetraalkylphosphorodiamidic chlorides in presence of triethylamine [4]. The constants of the compounds obtained are given in the table.

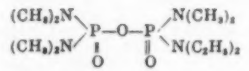
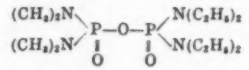
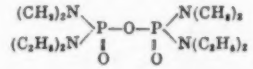
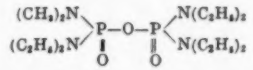
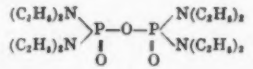
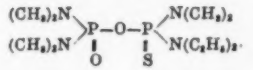
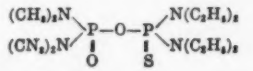
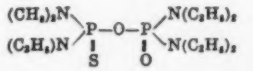
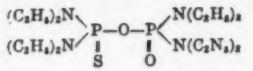
The substances listed in the table are high-boiling, almost colorless liquids of pungent odor. As compared with octamethylpyrophosphoramide, they have higher boiling points and refractive indices and lower densities. These compounds are insecticides: they function as stomach poisons.

In the determination of the molecular refractions of compounds of this type is was found that the experimental and calculated values do not agree: there are exaltations of about 1.7-1.8 units for the pyrophosphoramides and of 1.5, on the average, for the thiopyrophosphoramides (the AR of phosphorus was taken to be 3.76, and the AR of nitrogen was taken to be 2.744). It is probable that in this case, as has been done in some other cases [5], a more accurate value of AR for phosphorus or nitrogen must be found, but we found this to be impossible because of the paucity of factual material and a certain scatter in the values.

EXPERIMENTAL

Preparation of Octaalkylpyrophosphoramides and Octaalkylthiopyrophosphoramides. The acid chloride of the tetraalkylphosphorodiamidic or tetraalkylphosphorodiamidothioic acid was mixed with an equimolecular amount of the ethyl tetraalkylphosphorodiamidate, and the mixture was heated in a round-bottomed flask fitted with reflux condenser for 12-18 hours at 160-170°. The course of the reaction was followed and its completion determined from the amount of ethyl chloride liberated; the ethyl chloride was withdrawn at the free end of the reflux condenser. When the liberation of ethyl chloride stopped, the reaction mixture was cooled and vacuum-distilled.

Octaethylpyrophosphoramide and symmetrical tetraethyltetramethylpyrophosphoramide were prepared in a different way: the acid chlorides of tetraethyl- and diethyldimethyl-phosphorodiamidic acids were treated with water in presence of triethylamine for the binding of hydrogen chloride. When the reactants were mixed, no rise in temperature was observed. The mixture was warmed, the reaction was at 80-90° with stirring for 6-7 hours. The resulting thick mass was diluted with gasoline. Triethylamine hydrochloride was filtered off, gasoline was distilled off, and the residue was vacuum-distilled.

Formula of compounds	B. p. in °C (p in mm)	d_4^{20}	n_D^{20}	Yield (%)	P content (%)		MR	
					found	calc.	found	calc.
	132—133 (0,04)	1,1067	1,4625	32	19,65 19,60	19,71	78,07	79,54
	156—157 (2)	1,0851	1,4640	47,5	13,21 18,25	18,12	86,96	88,77
	153—155 (2)	1,0831	1,4630	40,9	18,09 18,18	18,12	86,97	87,77
	159—160 (1,5)	1,0627	1,4645	54	16,40 16,70	16,75	96,16	98,013
	174—176 (1)	1,0444	1,4650	30,4	15,58 15,70	15,6	105,505	107,249
	150—152 (2)	1,1178	1,4912	43,7	19,0 19,03	18,78	85,53	87,03
	128—131 (0,05)	1,0951	1,4928	30	16,98 16,92	17,32	94,97	96,22
	171—172 (1,5)	1,0754	1,4910	46	16,05 16,05	16,05	103,95	105,5
	159—161 (0,02)	1,0611	1,4900	48,3	15,03 15,11	14,92	112,90	114,73

Diethylhexamethylpyrophosphoramide was prepared from 36.35 g (0.18 mole) of diethyldimethylphosphorodiamidic chloride and 32.9 g (0.18 mole) of ethyl tetramethylphosphorodiamidate. The mixture was heated for 18 hours at 160-170°, and vacuum distillation from an Arbuzov flask than gave 18.4 g (32%) of diethylhexamethylpyrophosphoramide; b. p. 132-133°, (0.04 mm), $n^{20}D$ 1.4625, d^{20}_4 1.1067; found MR 78.07; calculated MR 79.54.

Found %: C 38.74, 38.75; H 8.98, 8.90; P 19.65, 19.60. $C_{10}H_{28}O_3N_4P_2$. Calculated %: C 38.2; H 8.91; P 19.71.

Tetraethyltetramethylpyrophosphoramide was prepared from 16 g (0.94 mole) of tetramethylphosphorodiamidic chloride and 22.1 g (0.94 mole) of ethyl tetraethylphosphorodiamidate. Reaction was at 160-170° for 16 hours. Vacuum distillation gave 15.2 g (47.5%) of tetraethyltetramethylpyrophosphoramide; b. p. 156-157° (2 mm); $n^{20}D$ 1.4640, d^{20}_4 1.0851; found MR 86.96; calculated MR 88.77.

Found %: C 41.67, 41.50; H 9.63, 9.55; P 18.21, 18.25. $C_{12}H_{32}O_3N_4P_2$. Calculated %: C 42; H 9.35; P 18.12.

Tetraethyltetramethylpyrophosphoramide (Symmetrical) was prepared from 20.5 g (0.29 mole) of diethyldimethylphosphorodiamidic chloride, 0.93 g (0.052 mole) of water, and 10.4 g (0.103 mole) of triethylamine by heating the mixture at 80° for eight hours. Vacuum distillation gave 13.9 g (40.9%) of tetraethyltetramethylpyrophosphoramide; b. p. 153-155° (2 mm), $n^{20}D$ 1.4630, d^{20}_4 1.0831, found MR 86.97; calculated MR 88.77.

Found %: C 41.70, 41.50; H 9.30, 9.28; P 18.09, 18.18. $C_{12}H_{32}O_3N_4P_2$. Calculated %: C 42; H 9.35; P 18.12.

Hexaethyldimethylpyrophosphoramide was prepared from 19.85 g (0.1 mole) of diethyldimethylphosphorodiamidic chloride and 23.6 g (0.1 mole) of ethyl tetraethylphosphorodiamidate. The mixture was heated at 160° for 16 hours. Vacuum fractionation gave 20 g (54%) of hexaethyldimethylpyrophosphoramide; b. p. 159-160° (1.5 mm); $n^{20}D$ 1.4645, d^{20}_4 1.0627; found MR 96.16; calculated MR 98.013.

Found %: C 45.33, 45.43; H 9.89, 9.80; P 16.40, 16.70. $C_{14}H_{36}O_3N_4P_2$. Calculated %: C 45.3; H 9.75; P 16.75.

Octaethylpyrophosphoramide was prepared from 45.3 g (0.2 mole) of tetraethylphosphorodiamidic chloride, 1.8 g (0.1 mole) of water, and 20.2 g (0.2 mole) of triethylamine. After removal of triethylamine hydrochloride, the residue was vacuum-distilled. The product, amounting to 16 g (40%), was octaethylpyrophosphoramide; b. p. 174-176° (1 mm); $n^{20}D$ 1.4650, d^{20}_4 1.0444; found MR 105.505, calculated MR 107.249.

Found %: P 15.58, 15.70. $C_{16}H_{10}O_3N_4P_2$. Calculated %: P 15.60.

Diethylhexamethylthiopyrophosphoramide was prepared from 40.7 g (0.19 mole) of diethyldimethylphosphorodiamidothioic chloride and 34.2 g (0.2 mole) of ethyl tetramethylphosphorodiamidate by heating the mixture at 170° for 18 hours. Vacuum distillation gave 27.3 g (43.7%) of product, $n^{20}D$ 1.4912, d^{20}_4 1.1178, found MR 85.53, calculated MR 87.03.

Found %: P 19.0, 19.03. $C_{10}H_{28}O_2N_4P_2S$. Calculated %: P 18.78.

Tetraethyltetramethylthiopyrophosphoramide was prepared from 24.25 g (0.1 mole) of tetraethylphosphorodiamidothioic chloride and 18.0 g (0.1 mole) of ethyl tetramethylphosphorodiamidate by heating the mixture at 170° for 18 hours. Vacuum distillation gave 10.8 g (30%) of tetraethyltetramethylthiopyrophosphoramide; b. p. 128-131° (0.05 mm); $n^{20}D$ 1.4928, d^{20}_4 1.0951, found MR 94.97, calculated MR 96.22.

Found %: C 40.37, 40.56; H 9.07, 9.09; P 16.98, 16.92. $C_{12}H_{32}O_2N_4P_2S$. Calculated %: C 40.22; H 8.92; P 17.32.

Hexaethyldimethylthiopyrophosphoramide was prepared by heating a mixture of 16.25 g (0.078 mole) of diethyldimethylphosphorodiamidothioic chloride and 17.85 g (0.075 mole) of ethyl tetraethylphosphorodiamidate at 170° for 24 hours. Vacuum distillation gave 13.2 g (46%) of hexaethyldimethylthiopyrophosphoramide; b. p. 171-172° (1.5 mm); $n^{20}D$ 1.4910, d^{20}_4 1.0754, found MR 103.95, calculated MR 105.5.

Found %: C 43.43, 43.36; H 9.38, 9.36; P 16.05, 16.05. $C_{14}H_{36}O_2N_4P_2S$. Calculated %: C 43.5; H 9.33; P 16.05.

Octaethylthiopyrophosphoramide was prepared by heating a mixture of 24.25 g (0.1 mole) of tetraethylphosphorodiamidothioic chloride and 23.6 g (0.1 mole) of ethyl tetraethylphosphorodiamidate for 17 hours. Vacuum distillation gave 20 g (48.3%) of octaethylthiopyrophosphoramide; b. p. 159-161° (0.02 mm), $n^{20}D$ 1.4900, d^{20}_4 1.0611, found MR 112.90; calculated MR 114.73.

Found %: P 15.03, 15.11. $C_{16}H_{40}O_2N_4P_2S$. Calculated %: P 14.92.

SUMMARY

Nine nitrogen-containing derivatives of pyrophosphoric and thiopyrophosphoric acids were synthesized, and some of their properties were studied.

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POLYMERIZATION AND COPOLYMERIZATION OF N-VINYL COMPOUNDS

COMMUNICATION 4. POLYMERIZATION OF N-VINYLPHTHALIMIDE

A. F. Nikolaev, S. N. Ushakov, and M. R. Rozenberg

The published information on the polymerization of N-vinylphthalimide is inadequate. An American patent of 1942 [1] states that N-vinylphthalimide can polymerize in the mass in presence of peroxides. In absence of catalyst no polymerization is observed; only when the temperature is raised to 200° does slow polymerization occur. Another patent [2] states that N-vinylphthalimide can be polymerized in emulsion.

The first paper on the subject appeared in 1944 [3], and this described a method of preparing polyvinylphthalimide in the mass in 61% yield. The process was carried out at 100° for 24 hours in presence of 0.5% of benzoyl peroxide (BP). According to Dennis [4], the resulting clear orange polymer had a softening point of 232° and was soluble only in phenol and dimethylformamide. In another paper [5] the solution polymerization of vinylphthalimide is described. An 85:15 mixture of 1,2-dichloroethane and methanol was used as solvent. Polymerization in presence of 0.5% of BP required 40 hours, and the polymer was precipitated from solution with alcohol as a white brittle fibrous product. The object of these investigations was the preparation of a vinylphthalimide polymer for further conversion into polyvinylamine by hydrolytic elimination of phthaloyl groups.

We now describe work on the mass and solvent polymerization of vinylphthalimide and report some of the properties of the polymer.

Mass Polymerization. Experiments on the mass polymerization of N-vinylphthalimide were carried out at 85° in presence of initiators, namely, BP and 2,2'-azobis[2-methylpropionitrile] (AN). The first experiments (Fig. 1, curve 1) already showed that in presence of 0.5% of BP vinylphthalimide polymerizes rapidly with formation of a transparent solid polymer. During the first hour the progress of reaction was nearly 80%, and it then continued at a low rate. When polymerization is rapid, much heat must be evolved with a resulting sharp rise in the temperature of the polymerization mixture, which will be associated with rapid decomposition of the initiator. We measured the rise in the temperature of the polymerization mixture in the ampoule. For this purpose 1 g portions of vinylphthalimide containing different amounts of initiator (BP) were placed in ampoules closed with stoppers carrying sealed-in thermometers. The ampoules were immersed in a water thermostat, and when they had attained the temperature of the thermostat (85 ± 0.1°), the temperature in the ampoule was read every 15 seconds. A similar method has been used in other investigations [6].

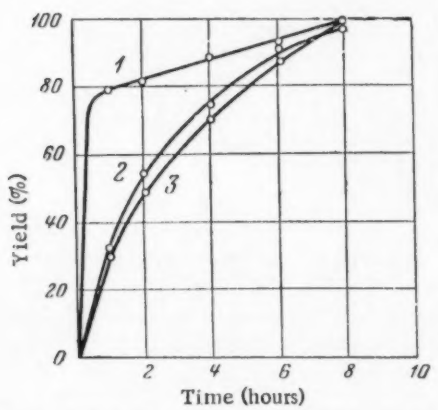

Fig. 1. Relation of yield of polyvinylphthalimide to duration of polymerization and nature of initiator at 85°: 1) 0.5% of BP; 2) 0.05% of BP; 3) 0.05% of AN.

The results of the experiments (Fig. 2) indicate that the process is highly exothermic and that polymerization is very rapid initially at BP concentrations of above 0.1%. The effect of initiator concentration on the yield and molecular weight (intrinsic viscosity) of the polymer is shown in Table 1.

Table 1 shows that the molecular weight of the polymer increases with increase in the duration of polymerization and a polymer having $[\eta] \geq 1.0$ is formed at BP concentrations of less than 0.1%. It was noted that when the mass polymerization of vinylphthalimide was prolonged and the yield of polymer was greater than 75-80°, insoluble polyvinylphthalimide was obtained. It was found also that drying of reprecipitated polymer above 110° or compression of polymer powder dried at 60-70°, e.g., for ten minutes at a pressure of 300 kg/cm² and a temperature of 250-280°, again leads to partial loss of solubility.

TABLE 1

Effect of Initiator Concentration on the Rate of Polymerization of N-Vinylphthalimide at 85°

Experiment	Amount of BP (%)	Yield of polymer (%)	Intrinsic viscosity $[\eta]$	Rate of polymerization (%)
Duration of polymerization 6 minutes				
1	1	60,0	0,075	10,00
2	0,5	41,5	0,195	6,91
3	0,25	31,0	0,245	5,16
Duration of polymerization 30 minutes				
4	1	69,0	0,390	2,30
5	0,5	52,0	0,525	1,73
6	0,25	36,0	0,700	1,20
7	0,1	21,5	0,990	0,71
8	0,05	17,5	1,200	0,58
9	0,01	9,0	1,235	0,30

These facts indicate the occurrence of secondary processes [7], both in the mass polymerization of vinylphthalimide, and in the polymer itself at high temperatures. These are accompanied by partial loss of solubility, probably due to cross-linking of the polymer chains. This process is probably the result of the opening of the phthalimide ring and the formation of bridging bonds between the macromolecules.

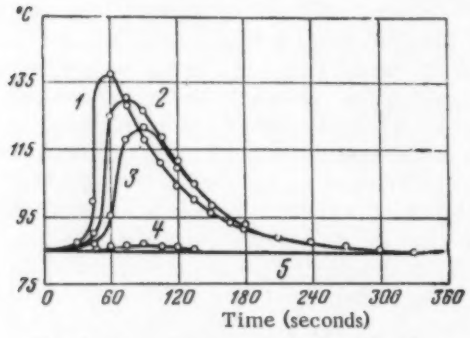

Fig. 2. Temperature curves for the polymerization of vinylphthalimide: 1) 1% BP; 2) 0.5 % BP; 3) 0.25% BP; 4) 0.1% BP; 5) temperature of thermostat.

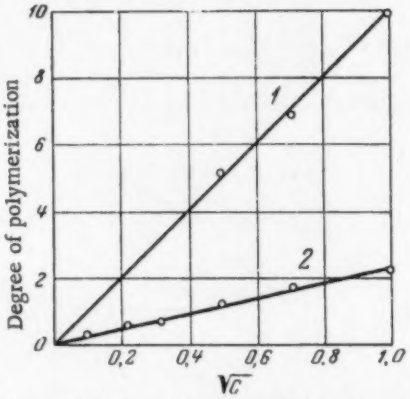

Fig. 3. Relation of the rate of the mass polymerization of vinylphthalimide at 85° to the square root of the initiator concentration: 1) mean rate over first 6 minutes; 2) mean rate over first 30 minutes.

From Fig. 3 is will be seen that the experimentally observed rate of polymerization is directly proportional to the square root of the initiator concentration at a given monomer concentration:

$$v = AC^{1/2}$$

in which v is the rate of polymerization; A is the constant; and c is the initiator concentration.

The straight lines representing this relation pass through the origin which indicates that, under the given reaction conditions, no polyvinylphthalimide is formed in absence of initiator, and that at all initiator concentrations the initial rate of polymerization is the greatest.

Comparison of the rates of polymerization of vinylphthalimide in presence of small amounts (0.05%) of BP and AN (Curves 2 and 3) shows that at this initiator concentration the rates of the process are almost the same. Complete conversion into polymer occurs in eight hours. At higher initiator concentrations, e.g., 0.5% and 1% it was found, however, that polymer is formed more rapidly in presence of AN than in presence of BP, and the molecular weight is higher. Thus, in 6 minutes at 85° the yield of polymer formed in presence of AN is 76% and $[\eta] = 0.33$, instead of 60% and $[\eta] = 0.075$ in presence of BP (1%).

Analogous behavior has been observed for other monomers, e.g., vinyl acetate [8], but not for methyl methacrylate. The almost identical effects of BP and AN at very low concentrations on the rate of polymerization of vinylphthalimide and the difference in their effects at high concentrations require further study for other monomers.

Solution Polymerization. Methanol, benzene, toluene, dichloroethane, and methylene chloride were used as solvents. Polymerization was carried out in ampoules at 65° in presence of 0.5% of BP; the proportions by weight of monomer to solvent were 1 : 2. The results (Table 2) indicate that benzene is the least active in chain transfer, because the polymer obtained in benzene has a higher molecular weight than those obtained in other solvents. The polyvinylphthalimide is precipitated from benzene and methanol as a white powder as it is formed. In methylene chloride and dichloroethane the polymer remains in solution.

TABLE 2

Polymerization of Vinylphthalimide in Various Solvents at 65°

Solvent	Yield of polymer (%)		$[\eta]$*
	3 hours	6 hours	
Methanol	10.0	29.7	0.075
Methylene chloride	20.6	53.1	0.120
Toluene	18.5	38.0	0.165
Dichloroethane	28.1	61.5	0.180
Benzene	24.5	56.7	0.420

* $[\eta]$ was determined for the 6-hour polymer.

TABLE 3

Solution Polymerization of Vinylphthalamide

Wt. ratio vinylphthalimide : benzene	Reaction temp. (° C)	Initiator (0.5%)	Yield of polymer (%)			$[\eta]$*
			3 hrs	6 hrs	9 hrs	
2,0	50	AN	45,0	63,0	79,0	0,600
1,0	50	AN	46,0	85,7	94,0	0,855
0,5	50	AN	43,0	82,2	92,0	0,540
0,25	50	AN	16,5	27,0	37,3	0,420
2,0	65	BP	28,1	41,2	55,0	0,223
1,0	65	BP	65,2	78,2	84,3	0,450
0,5	65	BP	34,5	50,1	66,0	0,430

* $[\eta]$ was determined for the 9-hour polymer.

The polymerization of vinylphthalimide was investigated in greater detail in benzene at 50° and 65° at an initiator (BP or AN) concentration of 0.5%. The results are shown in Table 3.

It will be seen from Table 3 that the rate of polymerization is at a maximum when the proportions by weight of vinylphthalimide and benzene are equal, and the resulting polymer has the highest molecular weight. For all the other proportions investigated the polymer is formed more slowly and has a lower molecular weight. These results, which were repeated several times, indicate the specific effect of benzene on the polymerization of vinylphthalimide. The observed relation cannot be explained solely from the point of view of the mechanism of chain transfer by benzene. In the polymerization of vinylphthalimide in benzene it is probable that their copolymerization occurs, as in the already described vinyl acetate – benzene system [9]. Some indication of this is given by the nitrogen content of the polymer obtained at a weight ratio of vinylphthalimide to benzene of 0.25; this was 7.45%, whereas the nitrogen content of pure polyvinylphthalimide should be 8.09%. A final conclusion on this matter will be possible after further study of the vinylphthalimide-benzene system.

TABLE 4
Some Properties of Polyvinylphthalimide

Method of polymerization			[η]	Softening point (° C)	Vicat thermostability (° C)	Brinell hardness (kg/mm²)	Water absorption in 24 hrs (%)
System	Temp. (° C)	BP (%)					
20% solution in dichloroethane	65	0,5	0,165	230	—	—	—
50% solution in benzene	65	0,5 AN	0,525	245	198	22 –23	0,38
In the mass	85	1,0	0,390	240	—	—	—
In the mass	85	0,5	0,475	245	198	—	—
In the mass	85	0,05	1,361	251	—	—	—

Experiments on the polymerization of vinylphthalimide in benzene show that the rate of the process in presence of 0.5% of AN, unlike that in presence of 0.5% of BP, is actually greater at a lower temperature (50° instead of 65°). The polymer formed has a higher molecular weight.

Table 4 gives some of the properties of polyvinylphthalimide prepared by various methods in presence of BP and AN.

Polyvinylphthalimide dissolves in phenol, dimethylformamide, and methylene chloride and swells in chlorinated hydrocarbons (chloroform, dichloroethane).

EXPERIMENTAL

N-Vinylphthalimide was synthesized and purified by the procedure that we have already described [10]. Before being used, benzoyl peroxide and 2,2'-azobis[2-methylpropionitrile] were recrystallized from methanol and dried to constant weight at 20° under a residual pressure of 10 mm. The solvents were dried and purified by distillation; the purity was checked by boiling point and refractive index (Table 5).

TABLE 5
Constants of Solvents

Solvent	B. p. (°C)	n_D^{20}
Methanol	64,5	1,3305
Benzene	80,0	1,5018
Dichloroethane	83,3	1,4440
Methylene chloride	40,0	1,4235
Toluene	110,3	1,4960

Polymerization in glass ampoules was carried out by a known procedure [11]. The polyvinylphthalimide was purified by two precipitations of its solution in methylene chloride by methanol. It was dried in a vacuum oven at 60° (10 mm). The relative viscosity of a 0.2% solution of the polymer in methylene chloride was determined at 20° in an Ostwald viscometer and was converted into intrinsic viscosity [η] by Billmeyer's eighth formula [12], which gives results in close agreement with the well-known graphical method of determining [η].

SUMMARY

1. An examination was made of the relation of the rate of polymerization of N-vinylphthalimide and of the molecular weight of the polymer to the conditions of mass or solution polymerization in presence of benzoyl peroxide or 2,2'-azobis[2-methylpropionitrile]. Polyvinylphthalimide of maximum molecular weight and softening point (245-251°) is obtained in the mass at an initiator concentration of less than 0.1% and a polymerization temperature of 85°, and in solution at an initiator concentration of less than 0.5% at 50-65°.

2. Polyvinylphthalimide is obtained in a powder form suitable for further processing by polymerization of the monomer in benzene.

3. The resulting polymer has adequate hardness, high thermostability (Vicat value 198°), and limited solubility in organic substances.

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KINETICS OF THE REACTION BETWEEN CUMENE HYDROPEROXIDE AND TRIETHYLENETETRAMINE IN PRESENCE OF IRON SALTS IN AQUEOUS SOLUTIONS

S. D. Razumovskii and S. S. Medvedev

In the manufacture of macromolecular materials, methods of initiating free-radical processes by means of oxidation-reduction reactions have recently found wide application. The most widely used oxidative components are peroxy compounds. Very suitable reducing agents for emulsion-polymerization processes have been found in polyethylenepolyamines of general formula

$$NH_2-(-C_2H_4NH-)_x-H$$

It was shown that polyethylenepolyamides readily promote polymerization in butadiene and styrene emulsions [1, 2]. The highest activity is possessed by amines containing amino groups substituted to different extents (primary and secondary or primary and tertiary) and separated by not more than two carbon atoms [3]. The reaction between amines and peroxides in organic media have been studied in some detail by Gambar'ian [4], Horner and co-workers [5], Grabak [6], and Imoto and co-workers [7]. The reactions of polyamines and peroxides in aqueous solutions have not received so much study. Ohrr and Williams [8, 9] showed that the reaction between cumene hydroperoxide (CHP) and triethylenetetramine, and also between some of their homologs, is of first order with respect to the peroxide and of zero order with respect to the amine and is considerably accelerated in presence of iron ions; they studied the effect of the pH of the solution and examined the formation of amine-iron complexes in detail. They suppose that pure amine and hydroperoxide do not react together, and the amine-iron complex becomes capable of such reaction as a result of the activation of the N–H bond. The amine is not capable of reducing ferric iron into ferrous.

The authors [8, 9] consider that the first stage of the reaction is expressed by the following equation:

$$ROOH + [RNH_2Fe^{++}] \rightarrow RO^{\cdot} + H_2O + R\dot{N}H + Fe^{++}.$$

Fe^{++} then forms a new complex, which can again take part in the reaction. The investigations that have been carried out do not fully explain the part played by iron in the reaction and the relation of reaction rate to iron concentration. It was of interest also to make a fuller kinetic investigation of the reaction between CHP and the polyamine. The present investigation was carried out with the object of elucidating these matters.

EXPERIMENTAL

Cumene hydroperoxide was prepared from its 40% solution in cumene by precipitation as the sodium salt in accordance with the described procedure [10]. The product used in this work contained 96-98% of active peroxide.

Technical triethylenetetramine was purified by fractionation at 3 mm. The 102-103.0° fraction was collected; it had $n^{20}D$ 1.4958 (the literature [11] gives $n^{20}D$ 1.4951).

Ferrous sulfate $FeSO_4$ of the "analytically pure" grade was reprecipitated twice from aqueous solution to remove the oxidized portion; it was vacuum-dried. The salt contained 99.5% of the theoretical amount of iron.

Ferric sulfate $Fe_2(SO_4)_3 \cdot 9H_2O$ was used as the "analytically pure" preparation; it assayed at 100.3% of the theoretical amount of iron.

The water used in the experiments was distilled twice in presence of alkaline permanganate.

Experimental Procedure

The reactions were carried out in a glass reactor of special design enabling the experiments to be carried out in an atmosphere of nitrogen, which was carefully purified from oxygen by means of cuprammonium solution. The design of the reactor will be seen from Fig. 1. Nitrogen was passed in through the tap 1. The outlet, which carried the tap 2, served for the evacuation of the reactor and the taking of test samples. In the taking of samples the reactor was removed from the thermostat and inverted; the necessary amount of solution was then removed through the tap 2 with constant passage of nitrogen into the reactor through the tap 1.

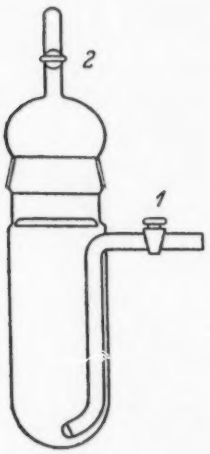


Fig. 1. Reactor.

Cumene hydroperoxide was estimated by the method of reduction at a dropping mercury electrode. The Heyrovsky micropolarograph was used. The polarographic cell was fitted for the passage of nitrogen through the solution under investigation. As supporting electrolyte we used 0.05 N HCl, because CHP scarcely reacts with the polyamine in acid solution and can be determined satisfactorily. A 0.5% gelatin solution was used to suppress oxygen maxima. In some experiments we used 0.1 N NaCl as supporting electrolyte. CHP was determined from the limiting current, which was attained at a potential of -0.32 v.

The colorimetric determination was carried out on an FM-1 universal photometer by comparison of the color of the investigated solution with the colors of a set of standard solutions differing in iron concentration. Ferrous iron was determined as the 1,10-phenanthroline complex. No analysis was carried out for the amine.

Experimental Results

By experiments on the reaction between CHP and triethylenetetramine in aqueous solution it was shown that reaction is rapid at low concentrations of iron salts (of the order of 10^{-6} mole/liter). Replacement of ferric iron by ferrous did not affect the reaction rate if the total iron content of the solution was kept constant. The rate of reaction between CHP and the polyamine depends greatly on the conditions under which the solutions of iron salts are prepared and kept. When iron solutions of concentration $4.23 \cdot 10^{-4}$ mole/liter and less were kept, their activities fell by about two-thirds in the first two or three hours. After one day no further change in catalytic activity occurred in the course of three months. In our further considerations we shall refer to such solutions of iron salts as "old" solutions.

It is known that aqueous solutions of iron salts are not stable; with keeping they change in color and conductivity, and the concentration of iron ions in the solution falls [12]. Study of the behavior of dilute iron solutions showed that the observed changes are associated with hydrolysis of the salts, the rate of which depends on the concentration, pH, and ionic strength of the solution [8]. It was found that for ferric chloride the rate of hydrolysis changes from $14.0 \cdot 10^{-6}$ to $0.014 \cdot 10^{-6}$ mole/liter $\cdot$ minute when the concentration changes from $0.133 \cdot 10^{-3}$ to $3.33 \cdot 10^{-3}$ moles/liter [13]. It follows that the catalytic activity of iron salts is greatly dependent on hydrolysis.

It was shown that ferric sulfate solutions having concentrations of $4.23 \cdot 10^{-3}$ mole/liter and over and kept for three months preserve maximum catalytic activity in the CHP-polyamine reaction. It was shown above that with increase in the concentration of the salt the rate of hydrolysis is greatly reduced. We are concerned, therefore, with a system which is not in equilibrium under the experimental conditions. On dilution of such solutions hydrolysis may be accelerated with reduction in catalytic activity.

Experiments with "Old" Iron Solutions

In these experiments the concentrations of CHP, amine, and iron were varied, which made it possible to determine the relation of the rate of reaction to the initial concentrations of all the reaction components. The

results of the experiments are presented in Figs. 2-4, from which it will be seen that the rate of reaction depends on the concentrations of the reactants. Study of this relation shows that reaction is of first order with respect to all the reactants, CHP, amine, and iron. In this connection, we must point out that at a concentration of more than $9.46 \cdot 10^{-8}$ mole/liter the rate of reaction does not depend on the amount of iron salt added (Fig. 2); in these cases precipitation of ferric hydroxide occurs. Analysis of the solutions showed that their iron contents did not exceed $9.46 \cdot 10^{-6}$ mole/liter, irrespective of the amount of salt added. In presence of triethylenetetramine the pH of the solution is 11.1, so that it is possible that a concentration of $9.46 \cdot 10^{-6}$ mole/liter is the limiting value for iron salts under the given conditions; above this value iron begins to be precipitated as hydroxide.

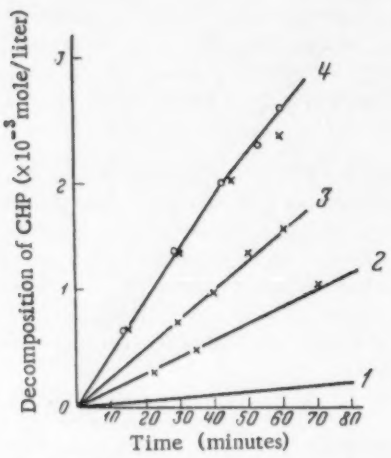


Fig. 2. Effect of concentration of ferric sulfate on reaction rate at 25° and at concentrations (mole/liter) of CHP $0.59 \cdot 10^{-2}$; polyamine $1.22 \cdot 10^{-2}$; $Fe_2(SO_4)_3$: 1) 0; 2) $2.23 \cdot 10^{-6}$; 3) $4.74 \cdot 10^{-6}$; 4) $9.46 - 47.3 \cdot 10^{-6}$.

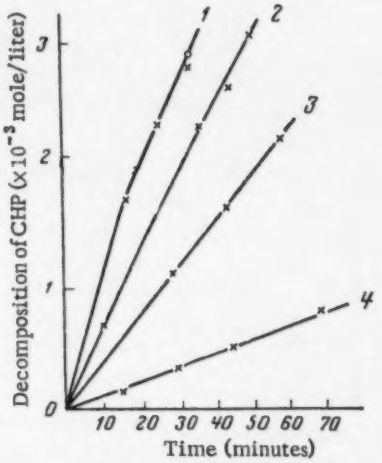


Fig. 3. Effect of concentration of the amine on reaction rate at 25° and at concentrations (mole/liter) of CHP $0.59 \cdot 10^{-2}$; $Fe_2(SO_4)_3$ $9.48 \cdot 10^{-6}$; amine: 1) $3.60 \cdot 10^{-2}$; 2) $2.40 \cdot 10^{-2}$; 3) $1.22 \cdot 10^{-2}$; 4) $0.24 \cdot 10^{-2}$.

We studied the temperature-dependence of the reaction rate. From the results we calculated the over-all activation energy for the reaction, which we found to be 10.3 kcal/mole.

Use of Fresh Iron Solutions

The concentrations of iron used in the experiments were only about one-thousandth of those which would ensure constant catalytic activity over a long time. Hence, the study of reaction in presence of iron salts which had not yet hydrolyzed presented great difficulty.

By strict observation of the procedure adopted in the mixing of the components, according to which the iron was added last, we succeeded in obtaining reproducible results and studying the effect of each reaction component on the reaction rate. The dependence of reaction rate on the initial concentrations of iron, amine, and CHP is shown in Figs. 5-7. The relationships are more complex than in the case of "old" iron solutions. The order of reaction with respect to iron changes suddenly at a concentration of $8.0 \cdot 10^{-6}$ mole/liter from 0.52 to 0.86. The rate of reaction gradually increases with increase in iron concentration until immeasurably high values are attained. There is no limiting rate, such as is characteristic for "old" iron solutions. The reaction order is 1 with respect to the hydroperoxide and 0.6 with respect to the amine over the concentration range studied. From the temperature-dependence of the reaction rate the over-all activation energy was calculated; it was found to be 4.5 kcal/mole.

It was of great interest to estimate the fraction of the CHP which decomposes by a chain mechanism under the action of free radicals formed in the primary reaction between CHP and the polyamine. Experiments with

nitric oxide showed that in aqueous solutions in an atmosphere of inert gas NO decomposes CHP very vigorously even in absence of amine. The use of water-soluble monomers did not give satisfactory results either. Methyl methacrylate, which has often been used before [8], polymerizes in the early stages of the reaction and is precipitated from solution with entrainment of considerable amounts of CHP, which makes study of the reaction very difficult. For these reasons we were unable to estimate the possible contribution of chain decomposition.

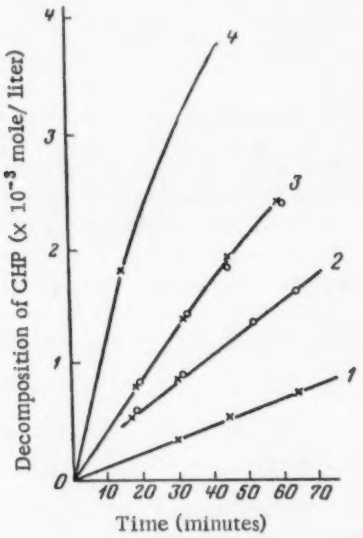


Fig. 4. Effect of concentration of CHP on reaction rate at 25° and at concentrations (mole/liter) of $Fe_2(SO_4)_3$ $9.48 \cdot 10^{-6}$; amine $1.22 \cdot 10^{-2}$; CHP: 1) $0.15 \cdot 10^{-2}$, 2) $0.30 \cdot 10^{-2}$, 3) $0.59 \cdot 10^{-2}$, 4) $1.17 \cdot 10^{-2}$.

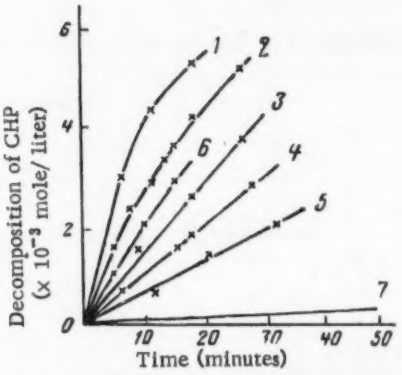


Fig. 5. Effect of iron concentration on reaction rate at 20° and at concentrations (mole/liter) of CHP $0.68 \cdot 10^{-2}$; amine $1.96 \cdot 10^{-2}$; $Fe_2(SO_4)_3$: 1) $21.3 \cdot 10^{-6}$, 2) $13.2 \cdot 10^{-6}$, 3) $5.30 \cdot 10^{-6}$, 4) $2.12 \cdot 10^{-6}$, 5) $1.06 \cdot 10^{-6}$, 6) $8.51 \cdot 10^{-6}$, 7) 0.

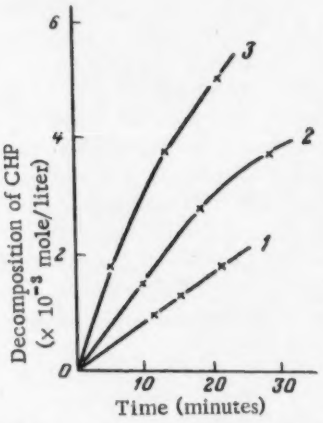


Fig. 6. Effect of the CHP concentration on the rate of the CHP-amine reaction at 20° and at concentrations (mole/liter) of amine $1.96 \cdot 10^{-2}$; $Fe_2(SO_4)_3$ $4.23 \cdot 10^{-6}$; CHP: 1) $0.30 \cdot 10^{-2}$, 2) $0.68 \cdot 10^{-2}$, 3) $1.08 \cdot 10^{-2}$.

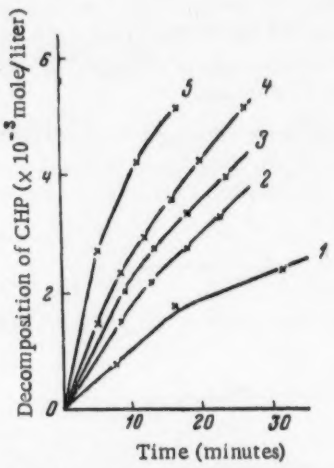


Fig. 7. Effect of initial amine concentration on reaction rate at 20° and at concentrations (mole/liter) of CHP $0.68 \cdot 10^{-2}$; $Fe_2(SO_4)_3$ $13.20 \cdot 10^{-6}$; amine: 1) $0.25 \cdot 10^{-2}$, 2) $0.49 \cdot 10^{-2}$, 3) $0.98 \cdot 10^{-2}$, 4) $1.96 \cdot 10^{-2}$, 5) $3.92 \cdot 10^{-2}$.

We have already pointed out the great effect of iron salts in the reaction between CHP and the polyamine. In absence of iron salts the reaction rate is very low. If to such a solution addition is made of a little of a substance that forms a stable complex with iron, e.g., sodium ethylenedinitrilotetraacetate (dissociation constant 10^{-39}), no reaction between amine and CHP is observed over a long period (the last analysis was made after three days). From this it may be inferred that reaction between CHP and amine does not occur in complete absence of iron.

* * *

In order to study the reducing action of triethylenetetramine, aqueous solutions of the amine and ferric sulfate were investigated for their contents of ferrous iron. Experiments were carried out in both acid and alkaline media. As reagents for the ferrous ion in an acid medium we used potassium ferricyanide and 1,10-phenanthroline, which gave colored compounds. For the detection of the ferrous ion in an alkaline medium we used dimethylglyoxime [14]. In all cases we detected the formation of the characteristically colored complexes indicating the presence of ferrous ions in the system. In an acid medium reduction is slow. Moreover, when the amine is added in an acid medium, the color of the thiocyanate complex with ferric ions disappears. If hydrogen peroxide is added to this system the color reappears. The amount of ferrous iron formed was estimated colorimetrically in an acid medium from the intensity of the color of the Fe^{++} – 1,10-phenathroline complex formed. The results are given in Table 1.

TABLE 1

$Fe_2(SO_4)_3$ conc. ($\times 10^{-5}$ mole/l)	Amine conc. ($\times 10^{-4}$ mole/l)	Fe^{++} found ($\times 10^{-4}$ mole/l)
3.38	4	1.05
3.38	4	1.15
3.38	6.4	1.90

It will be seen from Table 1 that change in the amine concentration causes changes in the concentration of reduced iron formed. Increase in the content of ferric salt results in an increase also in the concentration of ferrous ions. We are probably concerned here with an equilibrium reaction which may depend greatly on the pH of the solution. No quantitative study of reduction in an alkaline medium was made because of the considerable experimental difficulties.

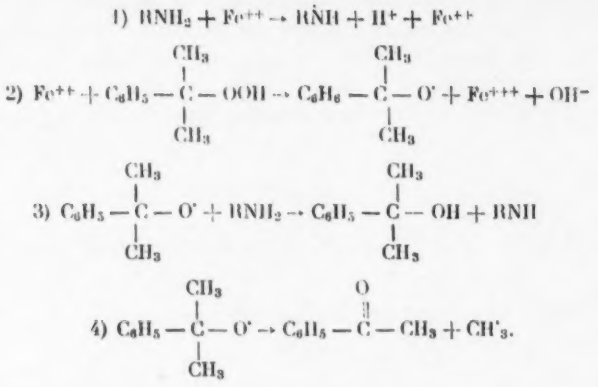
A qualitative investigation of the reaction products was carried out by methods described in the literature [15]. For analysis, the solution containing the reaction products was fractionated at reduced pressure. In the fraction of volatile organic substances we detected acetophenone $C_6H_5-\overset{\overset{O}{\|}}{C}-CH_3$ by its reaction with sodium nitroprusside, and α,α-dimethylbenzyl alcohol $C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$ with the aid of color reactions with mercuric sulfate and with vanillin.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental results for systems containing iron salts that had been subjected to preliminary hydrolysis are described by a kinetic equation in which all reactant concentrations appear with powers of unity:

$$W_p = K[CHP][RNH_2][Fe^{+++}].$$

Consideration of this equation together with the experiments on the reduction of ferric iron to ferrous by the amine and also the main reaction products enables us to suggest that the following reactions may occur in the system:



The radicals formed may take part in many reactions not shown in this scheme. Reaction (1) has a conditional character, for it is not known what products are formed from the amine as a result of its participation in the reduction. The representation of the reactions is based on some analogies in the literature [16-18].

Integration of the rate equation gives an expression for the amount of residual CHP as a function of time:

$$[CHP]_t = [CHP]_0 \cdot e^{-(K[Fe^{++}][RN_2]+\beta[RNH_2])t},$$

in which $[CHP]_0$ is the initial concentration of the hydroperoxide; K is the constant for the over-all reaction; and β is a correction factor which takes account of the iron content of the original substances.* The values of K and β were determined and found to be $K = 6.60 \cdot 10^4$ second^{-1} mole^{-1} and $\beta = 6.56 \cdot 10^2$ second^{-1}. Curves (Figs. 2-4) were calculated from this equation. The agreement between experimental and calculated points was good. The results of the calculations are given in Table 2.

TABLE 2

Comparison of Experimental Results with Values Calculated from the Integral Equation

Initial concn. (x 10^{-3} mole/liter) of		$Fe_2(SO_4)_3$ concn.	CHP that reacted in 20 min (x 10^{-3} mole/liter)		CHP that reacted in 40 min (x 10^{-3} mole/liter)	
CHP	polyamine		exptl. value	calc. value	exptl. value	calc. value
0,59	1,22	9,46	0,90	0,87	1,74	1,67
0,59	1,22	4,74	0,48	0,54	0,96	0,96
0,15	1,22	9,46	0,27	0,27	0,51	0,42
1,17	1,22	9,46	2,16	1,77	3,60	3,34

It is difficult to say where the difference lies between the reaction kinetics found when freshly prepared ferric sulfate solutions are used and those characteristic of solutions of iron salts that have undergone hydrolysis. We are inclined to see the cause of this not in the development of chain processes or in fundamental differences in mechanism, but in the differences in the conditions of the formation of amine-iron complexes and in the different relation to the pH of the solution. In our literature review we have already mentioned that in investigations on the reaction between hydroperoxides and polyamines in presence of iron ions the authors have supposed that the amine cannot reduce ferric ions to ferrous and that reaction proceeds as a result of the activation of the

* β is the intercept on the axis of ordinates of the curve for $W_p = f[Fe^{3+}]$.

N—H bond in the iron-amine complex [8, 9]. This view is not in accord with the known behavior of iron ions in analogous systems containing, for example, CHP, sugar, and iron pyrophosphate [19] or CHP, hydrazine, and iron ethylenedinitrilotetraacetate [20], or similar components [21].

It is known also that almost all oxidation-reduction systems are greatly activated by small additions of salts of metals of variable valence. It is here supposed that the metal ion takes part in the oxidation and reduction acts. It would be more correct, therefore, not to contrast the CHP-iron-amine system with the other analogous oxidation-reduction systems, but to place it in the general series, assuming that in this system iron is a catalyst acting as a carrier of an electron from reducing agent to oxidizing agent.

SUMMARY

1. The reaction between cumene hydroperoxide and triethylenetetramine proceeds only in presence of iron.

2. The activity of iron salts depends on the experimental conditions and its variation is probably to be explained by the hydrolysis of these salts.

3. It was shown that the amine is able to reduce ferric salts, both in acid and in alkaline media.

4. The order of the reaction was determined with respect to all the reaction components, and the activation energy was calculated for the over-all reaction.

5. A law was deduced for the change in the concentration of hydroperoxide with time, and the constants of the over-all reaction were calculated.

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HOMOGENEOUS DESTRUCTIVE HYDROGENATION OF TETRALIN AT HIGH PRESSURES OF HYDROGEN

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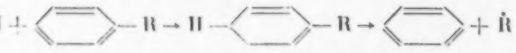
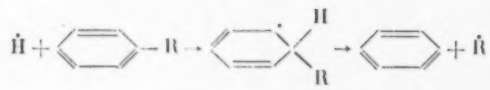
The present investigation forms a continuation of a series on the homogeneous destructive hydrogenation of aromatic hydrocarbons at high pressures of hydrogen [1-3]. In the papers cited we proposed a radical-chain scheme for the mechanism of this process in the case of alkylbenzenes. The scheme is based on the reaction of radicals formed in the thermal decomposition of alkylbenzenes with molecular hydrogen, and also with alkylbenzene molecules and reaction products. Reaction with hydrogen molecules leads to the formation of atomic hydrogen, which, in its turn, attacks a molecule of the alkylbenzene [4, 5] with formation of benzene and an alkyl radical (possibly also an alkane and a phenyl radical), which then continues the chain.

Darwent [5] suggested that this last reaction is based on addition of atomic hydrogen to an alkylbenzene molecule with formation of an unstable free radical, which then breaks down at the $C_{ar}-C_{al}$ bond:



(1)

It appears that the cleavage of this C–C bond is more probable when the hydrogen atom adds to a carbon atom of the ring which already carries a substituent:



(2)

In this case the $C_{ar}-C_{ar}$ bond will be re-formed in the stabilization of the radical with elimination of either a hydrogen atom with formation of the original particles or an R radical.* Semenov [6] gives some examples of some other substitution reactions which may also proceed by this mechanism.

We must point out that in alkylbenzenes the $C_{ar}-C_{al}$ bond is much stronger than, e.g., the C–C bond between the first and second carbon atoms of the side chain. Hence, the first stage of thermal decomposition, in particular that of ethylbenzene and cumene, leads to the formation of methyl radicals [7, 8]:

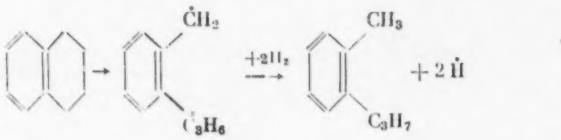
$$C_6H_5CH_2CH_3 \rightarrow C_6H_5\dot{C}H_2 + \dot{C}H_3 \quad (3)$$

$$C_6H_5CH(CH_3)_2 \rightarrow C_6H_5 - \dot{C}H - CH_3 + \dot{C}H_3 \quad (4)$$

However, in the homogeneous destructive hydrogenation of cumene increase in hydrogen pressure results in a considerable increase in the proportion of propane in the products and a reduction in the proportion of methane [3], which indicates the occurrence of a chain process with participation of atomic hydrogen in accordance with the scheme described above. Hence, at high pressures of hydrogen there is preferential cleavage of a C–C bond that is not the weakest in the original alkylbenzene molecule.

* It is probable that, in principle, a phenyl radical can be formed by the elimination of RH.

From this point of view the investigation of the homogeneous destructive hydrogenation of tetralin (1,2, 3,4-tetrahydronaphthalene) presents great interest. On analogy with alkylbenzenes it may be expected that the weakest bond in tetralin will be that between the first and second carbon atoms in the hydrogenated ring, so that its thermal decomposition should lead to the formation of the di-radical of o-propyltoluene $C_6H_4(\dot{C}H_2)(\dot{C}_3H_6)$. At high pressures of hydrogen a chain of reactions should occur with formation of butylbenzene:



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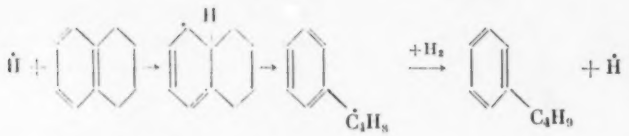


(6)

In its turn, butylbenzene will undergo further homogeneous destructive hydrogenation. There are indeed references in the literature to the formation of butylbenzene in the homogeneous destructive hydrogenation of tetralin. Thus, Hall [9] carried out this process at 450° at an initial hydrogen pressure of 100 atm, and he showed that the reaction products included benzene, toluene, ethylbenzene, and butylbenzene.

A kinetic investigation of the homogeneous destructive hydrogenation of tetralin was carried out by Nemtsov and co-workers [10]; they found that the kinetics of this process can be described approximately by the equation for a bimolecular reaction, and they calculated the activation energy (66 kcal/mole). The value of the pre-exponential factor in the Arrhenius equation was found to be 400 times as great as that calculated from the theory of active collisions, which is evidence in favor of a chain mechanism for the reaction (however, Nemtsov himself considered that a chain mechanism was not very likely). Nemtsov pointed out that the homogeneous destructive hydrogenation of tetralin is accompanied by its isomerization into methylindan. Similar isomerization had been earlier detected by Orlov and Likhachev [11]. Until now, however, it has not been shown which methylindan isomer is formed and to what relative extents the processes of isomerization and destructive hydrogenation occur. In the calculation of the rate constants for the homogeneous destructive hydrogenation of tetralin, Nemtsov was therefore compelled to start from data on the over-all reactions of tetralin in the two directions. The methods of investigation used in the researches cited did not permit the investigators to obtain full and exact information about the composition of the reaction products and, in particular, about the presence of o-dialkylbenzenes, about the position of the methyl group in the methylindan formed, and about the presence of alkylbenzenes having branched side chains.

As a result of the present investigation it is possible to answer these questions and to propose a general scheme for the transformations of tetralin under the conditions studied.

EXPERIMENTAL *

The tetralin used was prepared by the hydrogenation of naphthalene (purified with the aid of sodium) in presence of Raney nickel. After being vacuum-fractionated through a column of 30-plate efficiency the tetralin had the following properties: b. p. 207.5° (760 mm); 92.7-92.8° (20 mm); $n^{20}D$ 1.5414; d^{20}_4 0.9702; the literature [12] gives b. p. 207.57°; $n^{20}D$ 1.54135; d^{20}_4 0.9702.

The experiments were carried out in a stainless steel reactor (capacity about 120 ml, inclusive of the volume of the manometer) fitted with a hydraulic seal. The temperature was measured with a thermocouple in a steel pocket which passed through the hydraulic seal to the center of the reactor; the temperatures was maintained constant within ± 2°. In each experiment 35 g of tetralin was placed in the reactor, and hydrogen was passed in from a cylinder and through a boosting device to give an initial pressure of 100-600 atm; the electrical heater was then switched on. The duration of the experiment was counted from the moment the required temperature (440-462°) was attained until the heat was switched off.

* Laboratory worker M. V. Kazymova took part in this work.

The reaction products were fractionated through a column of 30-plate efficiency. A typical fractionation curve for a case in which homogeneous destructive hydrogenation of tetralin had proceeded to a fairly considerable extent is shown in the figure; horizontal sections corresponding to benzene (b. p. 80.1°), toluene (b. p. 110.6°), and ethylbenzene (b. p. 136.2°) can be seen clearly on the curve, and there are also two slightly inclined sections at 183-184° and 187-189°. The second of these corresponds to tetralin. The residue from the fractionation contained some naphthalene.

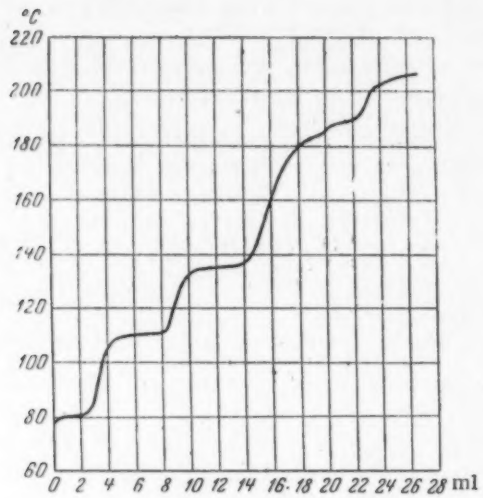


Fig. Fractionation curve for the product of Experiment 14 (462°, initial pressure of H_2 300 atm, τ = 3 hours).

We carried out a series of experiments at 462° and at an initial hydrogen pressure of 300 atm. Heating to the required temperature took 80 minutes. The pressure then attained was 630-660 atm. The pressure fell slowly: after three hours it had fallen by 90-100 atm, and after nine hours by 150-170 atm. Table 1 gives results of experiments at τ = 2, 3, 6, and 9 hours.

The results given in Table 1 show that with increase in the duration of the experiment the over-all conversion of the tetralin increases,* as also does the yield of the benzene fraction (b. p. up to 95°). The yields of the toluene (95-123°) and ethylbenzene (123-138°) fractions, and also of the 138-180° fraction, pass through a maximum. This indicates that the alkylbenzenes formed from the tetralin are subjected to further destructive hydrogenation. Investigation of the benzene fractions obtained in this series of experiments with the aid of Raman spectra enabled us to detect the presence of a little (about 3%) of cyclohexane. In the toluene fraction methylcyclohexane was apparently completely absent, or was present to an extent of less than 2%. The 109-112° fraction had $n^{20}D$ 1.4962-1.4965 (toluene has $n^{20}D$ 1.4969). By refractionation of the ethylbenzene fraction we obtained pure ethylbenzene having the following constants: b. p. 136.1-136.2°, $n^{20}D$ 1.4959; d^{20}_4 0.8675. The literature [12] give: b. p. 136.19°; $n^{20}D$ 1.4959; d^{20}_4 0.86702.

TABLE 1

Fractional Composition of the Products in Experiments at 462° and at an Initial Hydrogen Pressure of 300 Atm (Mean of Two Parallel Experiments, Expressed as Percent on the Original Tetralin)

B. p. of fraction (° C)	Expt. 15,19	Expt. 14, 20	Expt. 17, 18	Expt. 21, 22
	2 hours	3 hours	6 hours	9 hours
up to 95°	2,4	8,4	15,1	20,7
95—123	9,2	14,3	15,2	13,9
123—138	7,2	13,1	14,7	13,9
138—180	7,8	10,2	9,2	6,3
180—185	10,2	5,4	4,5	1,7
185—190	11,5	6,5		
190—200	3,5	2,0	4,6	2,6
200—207,5	26,1	10,3		
Residue	10,6	7,5	7,4	7,1
Distillation losses	1,2	2,9	1,6	2,1
Total	89,7	80,6	72,3	68,3

* The amount of unchanged tetralin was estimated from the yield of the 200-207.5° fraction.

The 138-190° fraction (amount taken: 63.36 g) was refractionated through a column of 50-plate efficiency. The narrow fractions obtained were investigated by the Raman-spectrum method.

The Raman spectra were recorded photographically. The apparatus and the methods of obtaining and measuring the spectra have been described previously [13]. In the identification of the hydrocarbons, to a large extent use was made of spectra obtained, also photographically, by two of the authors of the present paper* or at the Optical Laboratory of the Institute of Physics of the Academy of Sciences [14]. The spectra of o-propyltoluene, o-cumene, tert-butylbenzene, and o-diethylbenzene were taken from the literature [15, 16].

As already pointed out [13], in several cases the frequencies of spectrum lines given in [15] and [16] differ appreciably from our values; the intensities of the lines cannot always be recalculated to our scale with sufficient accuracy [15], and in some cases [16] only visual estimates are given. It is therefore necessary not to overestimate the accuracy of the quantitative analysis of fractions containing hydrocarbons whose spectra are known only from the literature. The predominance of aromatic hydrocarbons in all the fractions investigated excluded the possibility of detecting and identifying paraffins and cycloalkanes in nearly all cases. Our quantitative results, therefore, characterize only the relative amounts of aromatic hydrocarbons in the fractions. It should be noted, however, that the refractive indices of the fractions indicate that the contents of paraffins and cycloalkanes were extremely small. Table 2 gives the results of the analysis of ten fractions of b. p. 136.1-183.9°.

TABLE 2

Hydrocarbon Compositions of Fractions (%)

Hydrocarbon	Fraction									
	136.1—140.0°, 6.23 g n_D^{20} 1.4956	140.1—148.0°, 1.97 g n_D^{20} 1.4943	141.1—155.0°, 2.42 g n_D^{20} 1.4919	155.1—161.0°, 3.52 g n_D^{20} 1.4912	161.1—169.0°, 1.87 g n_D^{20} 1.4916	169.1—175.0°, 3.01 g n_D^{20} 1.4949	175.1—180.0°, 3.90 g n_D^{20} 1.5075	180.1—183.1°, 5.90 g n_D^{20} 1.4968	183.2°, 8.50 g n_D^{20} 1.4898	183.3—183.9°, 7.24 g n_D^{20} 1.4900
Ethylbenzene	~100	50								
o-Xylene	<2	5	~1							
Cumene		45	70	40						
Propylbenzene			30	57	95	5				
o-Ethyltoluene				~3	~5					
sec-Butylbenzene						80	75			
o-Cymene						<3	<6			
Indan						10	18	12		
Butylbenzene								85	90	90
o-Propyltoluene						<2	<3	<3		
trans-Decalin									2—4	2—4
1-Methylindan									5—10	5—10

The following conclusions can be drawn from data in Table 2:

1. The major components found in 136.1-183.9° fractions were: ethylbenzene (16%), cumene (9%), propylbenzene (10%), sec-butylbenzene (12%), butylbenzene (43%), indan (4%), and 1-methylindan (2-4%).

2. The following were present in very small amount: o-ethyltoluene (about 0.5%), o-xylene (≤ 0.5%), trans-decalin (0.5-1%), o-cymene (≤ 0.7%), and o-propyltoluene (≤ 0.8%). The reliability of the detection of the last two hydrocarbons is not so great as in the other cases.

The constants of the fraction boiling at 183.2° were found to be very close to those of butylbenzene ($n^{20}D$ 1.4898; d^{20}_4 0.8625). The literature [12] gives: $n^{20}D$ 1.48979; d^{20}_4 0.86013.

* The spectra of 1- and 2-methylindans were studied specially; they will be published elsewhere.

TABLE 3
Effect of Pressure on the Fractional Composition of the Reaction Products (% on Original Tetralin)

B. p. of fraction (° C)	440°, 5 hours				462°, 3 hours							
	Expt. 7		Expt. 9		Expt. 8		Expt. 25, 26		Expt. 14, 20		Expt. 23, 24		Expt. 27, 28	
	P_{max} 100 atm P_{max} 200 atm		P_{max} 300 atm P_{max} 610 atm		P_{max} 500 atm P_{max} 1020 atm		P_{max} 100 atm P_{max} 200 atm		P_{max} 300 atm P_{max} 610 atm		P_{max} 500 atm P_{max} 1020 atm		P_{max} 600 atm P_{max} 1200 atm	
Up to 95	0	0	0,6		8,4		0		8,4		20,6		23,7	
95—123	0	0	5,7		11,9		7,1		14,3		13,4		11,8	
123—138	0	4,1	4,5		9,6		6,9		13,1		11,4		10,2	
138—180	4,1	4,9	4,8		9,6		6,4		10,2		9,0		7,6	
180—185	4,9	5,7	17,3		15,6		4,9		5,4		3,9			
185—190	5,7	2,4	7,0		3,3		14,9		6,5				4,6	
190—200	2,4	63,8	2,3	31,9	12,6		4,7		2,0		4,6			
200—207,5	63,8	9,7	31,9	12,4	8,9		29,3		10,3				4,4	
Residue	9,7	3,0	12,4	4,2	3,6		15,0		7,5		4,1		2,0	
Distillation losses	3,0		4,2				1,6		2,9		1,5			
Total	93,6		90,7		83,5		89,8		80,6		68,5		64,3	

The main component found in the higher-boiling fraction (185-190°) was 1-methylindan, and some butylbenzene, 2-methylindan (5-10%), and trans-decalin (1-3%) were also present. No o-diethylbenzene was detected among the reaction products. It must be pointed out that the results on the contents of o-propyltoluene and o-cymene (Table 2) are conditional in character in that they indicate upper limits of the contents of these hydrocarbons. We were unable to obtain more definite results because of the complex character of the spectra.

Hence, in the 136.1-190° fractions we established the presence of ethylbenzene, o-xylene, cumene, propylbenzene, o-ethyltoluene, sec-butylbenzene, butylbenzene, indan, 1-methylindan, 2-methylindan, and trans-decalin; with less certainty we detected also o-cymene and o-propyltoluene.

By refractionation under reduced pressure the 183.9-190° fraction (18.51 g) gave a narrow fraction of b. p. 82.2° (20 mm) and having n^{20}_4 1.5253; and d^{20}_4 0.9377. For 1-methylindan the literature [17] gives: b. p. 189.5° (739.2 mm); $n^{25}D$ 1.5241; and d^{25}_4 0.9384.

Found %: C 90.94; H 9.05. $C_{10}H_{12}$.
Calculated %: C 90.90; H 9.09.

The 190-200° fraction (Table 1) contained 1-methylindan, trans-decalin, and tetralin; no cis-decalin was detected.

To construct a general scheme for the transformations of tetralin under the conditions studied on the basis of our results it was necessary to determine whether butylbenzene is formed directly from tetralin or is a product of the destructive hydrogenation of 1-methylindan. If butylbenzene is formed from tetralin through the intermediate stage of isomerization into 1-methylindan, then with increase in the duration of the experiment the yield of butylbenzene should increase and that of 1-methylindan should pass through a maximum, i.e., the ratio of these yields should change.*

TABLE 4
Ratio of Yields of the 180-185° and 185-190° Fractions

Temperature (° C)	τ (hours)	Initial hydrogen pressure (atm)		
		100	300	500
440	5	0.9	2.5	4.7
462	3	0.3	0.8	—

* These considerations apply when subsequent destructive hydrogenation of these two hydrocarbons occurs to an insignificant extent.

Experimental verification showed that this ratio remains almost constant. We carried out two pairs of parallel experiments at 440° at $\tau = 2$ and 5 hours at an initial hydrogen pressure of 250 atm. Under these conditions 19.6% and 38.6% of the tetralin reacted, respectively (calculated from the yield of the 200-207.5° fraction); only 1.0% and 4.9%, respectively, were obtained of products boiling below 180°. The ratios of the yields of fractions of b. p. 180-185° and 185-190° were 1.43 at $\tau = 2$ hours and 1.60 at $\tau = 5$ hours, i.e., remained almost unchanged; on the basis of Raman spectra, the ratio of the yields of butylbenzene and 1-methylindan was $\sim 2 (\pm 0.2)$ in both experiments. These results enable us to affirm that the isomerization of tetralin into 1-methylindan and the destructive hydrogenation of tetralin with formation of butylbenzene are processes which proceed simultaneously. The constancy of the relative amounts of the 180-185° and 185-190° fractions was observed by us in other series of experiments also.

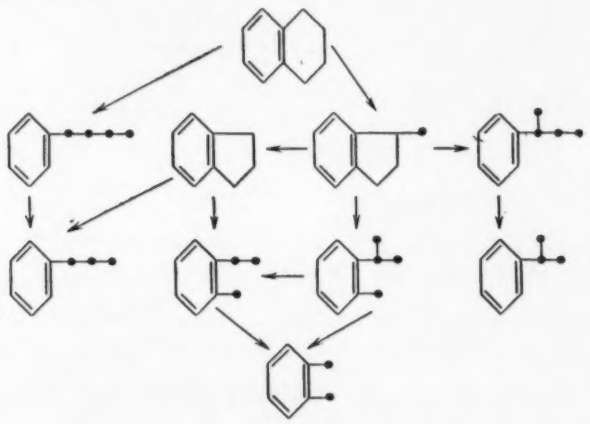
Table 3 gives results on the effect of pressure on the course of the homogeneous destructive hydrogenation of tetralin at 440° and 462°.

From Table 3 we may conclude that increase in pressure accelerates homogeneous destructive hydrogenation very considerably. Increase of initial hydrogen pressure from 300 to 500 atm at 462° and $\tau = 3$ hours resulted in about the same increase in the over-all conversion of tetralin as increase in the duration of the experiment from 3 to 6 hours at 300 atm (Table 1). However, for a given over-all conversion of tetralin the yield of benzene was always found to be somewhat higher when the experiment was carried out at a higher pressure [see Experiments 15, 19 (Table 1) with Experiments 25, 26 (Table 3), and also Experiments 17, 18 (Table 1) with Experiments 23, 24 (Table 3)]. This indicates also the effect of hydrogen pressure on the composition of the products of the process.

The effect of pressure becomes particularly notable when we compare the ratios of the yields of the butylbenzene (180-185°) and 1-methylindan (185-190°) fractions at various pressures (Table 4).

The maximum yields of butylbenzene and 1-methylindan obtained were about 20% and 10%, respectively, on the original tetralin. Table 4 shows that the ratio of the yields of these fractions increases rapidly with rise in pressure and with lowering of temperature. This probably indicates that the activation energy for the isomerization of tetralin into 1-methylindan is greater than that for the homogeneous destructive hydrogenation of tetralin. It may be supposed also that the rate of isomerization of tetralin, if indeed it does increase with increase in pressure,* increases much more slowly than the rate of destructive hydrogenation with formation of butylbenzene. Hence, under the conditions studied, tetralin undergoes transformations in two main directions (isomerization into 1-methylindan and transformation into butylbenzene) characterized by different temperature-dependence and pressure-dependence of reaction rate.

The results of the present investigation enable us to propose the following general radical-chain scheme for the transformations of tetralin under the conditions studied. Initiation of chains arises from the cleavage of the weakest C—C bond in the hydrogenated ring of tetralin (this being apparently the bond between the first and second carbon atoms) with formation of di-radicals. The reaction of these with hydrogen and the subsequent reactions of atomic hydrogen finally lead to the formation of butylbenzene in accordance with equations (5) and (6). Isomerization of tetralin to 1-methylindan proceeds simultaneously. In their turn, butylbenzene and 1-methylindan undergo destructive hydrogenation (see Scheme).



* The results of Experiments 7 and 9 (Table 3) may indicate some increase in rate of isomerization with increase in pressure.

The scheme does not show the formation of ethylbenzene, toluene, and benzene, nor of 2-methylindan, trans-decalin, naphthalene, and cyclohexane. Ethylbenzene can be formed from butylbenzene, sec-butylbenzene, propylbenzene, and cumene; also, possibly, from o-ethyltoluene.

We have no information to indicate whether 2-methylindan is formed by the isomerization of 1-methylindan or directly from tetralin. It should be noted that the destructive-hydrogenation product characteristic for 2-methylindan (isobutylbenzene) was not detected among the reaction products. The origins of the other substances indicated in the scheme will be obvious. It is noteworthy that in the homogeneous destructive hydrogenation of 1-methylindan preferential cleavage of the $C_{ar}-C_{al}$ bond more remote from the methyl group appears to occur with formation of sec-butylbenzene. The primary process in the thermal decomposition of 1-methylindan is evidently the formation of the di-radical of o-cymene.

Hence, the results of the investigation favor the views expressed at the beginning of the paper on the mechanism of the homogeneous destructive hydrogenation of aromatic hydrocarbons.

SUMMARY

1. The homogeneous destructive hydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) was investigated at 440-462° and at pressures of up to 1200 atm.

2. A general scheme is proposed for the transformations of tetralin under the conditions studied; it is based on the investigation of the reaction products by fractional-distillation and Raman-spectrum methods, and also on kinetic data.

3. The results are in accord with the views expounded in the paper on the radical-chain mechanism of the homogeneous destructive hydrogenation of aromatic hydrocarbons.

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VINYL ETHERS

COMMUNICATION 7. ION- AND RADICAL-INDUCED HOMO- AND CO-POLYMERIZATION OF VINYL ETHERS OF CYCLOHEXANOL, DECAHYDRO-2-NAPHTHOL, AND 2-NAPHTHOL

A. V. Bogdanova, M. F. Shostakovskii, and G. K. Krasil'nikova

Study of the properties and reactions of vinyl ethers containing cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl groups has revealed their interesting property of undergoing homo- and co-polymerization by ionic and free-radical mechanisms. While providing a comparison of the chemical properties of the original vinyl ethers in their dependence on the groups present, this reaction is a source of products of value in applied chemistry. In earlier papers [1-3] we described the polymerization of phenyl and p-tert-butylphenyl vinyl ethers and their co-polymerization with ethyl and butyl vinyl ethers. It was noted also [4-7] that cyclohexyl and decahydro-2-naphthyl vinyl ethers have high tendencies to polymerize under the action of ionic catalysts. The patent literature [6] indicates the polymers and copolymers of these ethers have found a variety of applications in industry. Thus, "Igevin C" contains a copolymer of decahydro-2-naphthylvinyl ether and is used in the manufacture of leather substitutes and, in admixture with paraffin and bitumins, for the impregnation of paper. "Igevin AO-28" contains 80% of decahydro-2-naphthyl vinyl ether polymer and is used as an ingredient of self-hardening lacquers. "Igevin Z" contains a decahydro-2-naphthyl vinyl ether polymer and is a substitute for natural solid resins. "Igevin IZ" contains 40% of decahydro-2-naphthyl vinyl ether and is used for the finishing of leather straps. From the products enumerated, auxiliary products are prepared for the manufacture of leather, train oil substitutes, wool fat, and castor oil. The polymers from cyclohexyl and decahydro-2-naphthyl vinyl ethers are used in "ageronal dispersions," in oil additives, as thickeners for cable oil, etc.

There are no references in the literature to the polymerization of 2-naphthyl and decahydro-2-naphthyl vinyl ethers in presence of 2,2'-azobis[2-methylpropionitrile]. It is known only that phenyl and p-tert-butylphenyl vinyl ethers may polymerize in presence of this initiator and may copolymerize with alkyl vinyl ethers [8], and that, under certain conditions the azo nitrile will bring about the polymerization of isopropyl and cyclohexyl vinyl ethers [9]. Shostakovskii and Khomutov [10] obtained methyl methacrylate copolymers of butyl and phenyl vinyl ethers in presence of benzoyl peroxide. It is known from the patent literature that such copolymers can be applied in the preparation of water-stable lacquers [5].

This paper is devoted to the study of the conditions required for the homo- and co-polymerization of 2-naphthyl, decahydro-2-naphthyl, and cyclohexyl vinyl ethers under the action of BF_3, benzoyl peroxide, and 2,2'-azobis[2-methylpropionitrile]. In the course of this study it was noted that, in presence of BF_3 at room temperature, 2-naphthyl vinyl ether polymerizes with greater difficulty than decahydro-2-naphthyl, cyclohexyl, and even phenyl vinyl ethers, but the ethers studied copolymerize very readily with alkyl vinyl ethers under these conditions. In accordance with this, the copolymerization of 2-naphthyl vinyl ether with phenyl vinyl ether required more severe conditions. It was found possible to prepare such copolymers of various compositions by varying the original proportions of monomers. Study of the conditions for free-radical polymerization showed that decahydro-2-naphthyl vinyl ether polymerizes to an appreciable extent in presence of not less than 1% of the azo nitrile and with increase in the amount of initiator the yield of polymer increases. In amounts of up to 0.5%, benzoyl peroxide does not bring about the polymerization of decahydro-2-naphthyl and cyclohexyl vinyl ethers; appreciable polymerization begins in presence of 5-6% of this initiator when treatment is at 80° for five hours with subsequent standing for 1-2 months at room temperature. By the thermal polymerization of cyclohexyl vinyl ether a white solid was obtained.

In the investigation of the conditions for copolymerization of the ethers under study with methyl esters of acrylic and methacrylic acids it was found that, with the exception of 2-naphthyl vinyl ether, they readily copolymerized with the acrylic and methacrylic esters with formation of copolymers of various compositions (Table 4). The compositions of the copolymers were calculated from the results of elementary analysis. In this case such a method of calculation is quite reliable, because the difference in carbon content between the phenyl vinyl ether and the acrylic esters is 20-30%. The observations showed that with increase in the vinyl ether content of the original mixture the yield of copolymer falls, but its content in the final product increases. This increase slows down, and for phenyl vinyl ether a limit appears to be reached at an original ratio to acrylic ester of 2:1. An excess of phenyl vinyl ether (ratio 3:1) gives a small increase in its content in the copolymer because polymerization is retarded to such an extent that the acrylic ester itself does not polymerize completely.

Comparison of the conditions for polymerization and copolymerization and also of the compositions of the resulting copolymers makes it possible to arrange the ethers in the following order of reactivity in these processes: butyl > decahydro-2-naphthyl > cyclohexyl > phenyl > 2-naphthyl vinyl ether.

EXPERIMENTAL

Polymerization of 2-Naphthyl, Decahydro-2-Naphthyl, and Cyclohexyl Vinyl Ethers in Presence of the BF_3-Ether Complex

The vinyl ethers were purified by the procedure developed in the Vinyl Compounds Laboratory [10] and had the following constants: cyclohexyl vinyl ether, b. p. 148°, $n^{20}D$ 1.4541; d^{20}_4 0.888; decahydro-2-naphthyl vinyl ether, b. p. 95° (6 mm), $n^{20}D$ 1.4880; d^{20}_4 0.9522; 2-naphthyl vinyl ether, b. p. 102-103° (2 mm), $n^{20}D$ 1.6150; and m. p. 35°.

The necessary amount of a 5% solution of the BF_3-ether complex in ether was added to a weighed amount of the vinyl ether in a three-necked flask fitted with stirrer, thermometer, and reflux condenser; this resulted in a rise of temperature. The viscous product was dissolved in ether, potassium carbonate was added to neutralize the catalyst, and the mixture was stirred for one hour; the solution was then filtered, and the polymer was precipitated from it by addition of methanol. After being reprecipitated, the polymer was dried in a vacuum desiccator at 50-60° (10-15 mm). The yields and characteristics of the polymers are given in Table 1; their solubilities are indicated in Table 2.

TABLE 1

Polymerization of Cyclohexyl, Decahydro-2-Naphthyl, and 2-Naphthyl Vinyl Ethers in Presence of BF_3

Ether	Polymerization temp. °C		Drops of BF_3 etherate for 0.1 mole of ether	Yield of polymer (%)	Molecular weight		Softening point (° C)	Appearance of polymer
	initial	maximum			found	calc.		
Cyclohexyl vinyl	2	120	5	95,00	499,1; 497,3	504,76 for $(C_8H_{14}O)_4$	97—102	White solid
"	19	110	5	95,70	699,4; 698,0	757,14 for $(C_8H_{14}O)_6$	99—110	White solid
Decahydro-2-naphthyl vinyl	2	135	5	93,00	1446,3; 1458,0	1442,32 for $(C_{12}H_{20}O)_8$		Slightly yellowish
"	20	130	5	89,00	2031,0; 1919,2	1983,19 for $C_{12}H_{20}O)_{11}$	92—97	Slightly yellowish
2-Naphthyl vinyl	20	120	9—10	79,00	640,9; 657,9	680,84 for $C_{12}H_{10}O)_4$	136	Greenish solid

Polymerization of 2-Naphthyl Vinyl Ether. 2-Naphthyl vinyl ether (12 g) was polymerized as described above in presence of the BF_3-ether complex. The viscous product was dissolved in ether, the catalyst was neutralized, and the mixture was treated with steam. We isolated 2.60 g of 2-naphthyl vinyl ether monomer and 9.50 g (79%) of its polymer. After being reprecipitated and vacuum-dried, the polymer had the constants given in Tables 1 and 2.

TABLE 2
Solubilities of Polymers Obtained

Solvent	Cyclohexyl vinyl ether polymer	Decahydro-2-naphthyl vinyl ether polymer	2-Naphthyl vinyl ether polymer
Diethyl ether	+	+	+
Acetone	+	–	+
Methyl alcohol	–	–	–
Ethyl alcohol	–	–	–
Propyl alcohol	–	–	–
Butyl alcohol	+ difficultly	–	+
Benzene	+	+	+
Dioxane	+	+	+
Petroleum ether	+	+	–
Gasoline	+	+	–

Copolymerization of Cyclohexyl, Decahydro-2-Naphthyl, and 2-Naphthyl Vinyl Ethers With Other Vinyl Ethers in Presence of BF_3

A mixture of definite molecular proportions of the monomers was placed in the previously described apparatus. The mixture was stirred while 5% BF_3 etherate was added gradually. The temperature of the mixture rose. In order to determine the end of the reaction, another portion of catalyst was added. The crude polymer was treated in the usual way; after two reprecipitations it was characterized (Table 3).

TABLE 3
Characteristics of Copolymers

Original vinyl ethers	Molar ratio of ethers taken	Elem. comp. of copolymer (%) C	Elem. comp. of copolymer (%) H	Mol. wt. of copolymer	Yield of copolymer (%)	Ratio of monomers in copolymer (%)	Notes
Cyclohexyl + butyl vinyl ethers	1 : 1	73,55 73,61	11,59 11,57	1608,0 1697,0	79,0	36,7 : 63,3	Colorless, very viscous and sticky
Cyclohexyl + phenyl vinyl ethers	1 : 1	76,93 76,77	10,13 10,13	1053,0 1068,0	60,7	76,06 : 12,5	Pale yellow, m.p. 55-60°
2-Naphthyl + ethyl vinyl ethers	1 : 1	72,87 72,77	9,40 9,20	1117,0 1166,3	31,0	17,8 : 82,2	Viscous
2-Naphthyl + ethyl vinyl ethers	1 : 2	69,00 69,20	10,37 10,30	1318,0 1299,0	48,0	2,60 : 97,40	Yellow
2-Naphthyl + phenyl vinyl ethers	1 : 2	82,10 82,24	6,63 6,53	597,00 597,10	41,0	37,6 : 62,4	Pale yellow, m.p. 63°
Decahydro-2-naphthyl + butyl vinyl ethers	1 : 1	76,10 76,33	11,52 11,61	2145,7 2088,4	—	38,1 : 61,9	Colorless viscous

Homo- and Co-polymerization of 2-Naphthyl, Cyclohexyl, and Decahydro-2-Naphthyl Vinyl Ethers in Presence of Free Radical Initiators

1. Polymerization of 2-Naphthyl and Decahydro-2-naphthyl Vinyl Ethers in Presence of 2,2'-Azobis[2-methylpropionitrile]. A mixture of 100 g of 2-naphthyl vinyl ether and 4 g of 2,2'-azobis[2-methylpropionitrile] was sealed in five ampoules (20 g of the ether and 0.8 g of the catalyst in each) and was heated continuously for 100 hours in a thermostat at 60°. The contents of the ampoules were treated with steam in order to distill off the monomer. The polymer was reprecipitated and dried. The yield of polymer (a white solid) was 5.6 g (5.6%).

Found %: N 2.37, 2.33. $C_{68}H_{62}O_5N_2$. Calculated %: N 2.83.

Decahydro-2-naphthyl vinyl ether was polymerized under the same conditions. The characteristics of the polymers obtained are given in Table 4.

TABLE 4

Polymerization of 2-Naphthyl and Decahydro-2-Naphthyl Vinyl Ethers in Presence of 2,2'-Azobis[2-methylpropionitrile]

Ether	Amt. azo nitrile (%)	Yield of polymer (%)	Mol. wt. of polymer	Softening point (° C)	Appearance of polymer
2-Naphthyl vinyl	4	5,6	902,6; 916,7	133—137	White solid
Decahydro-2-naphthyl vinyl	3	12,7	1601; 1640	94—102	White solid
Ditto	5	22,3	1098; 1079	80—85	White solid

TABLE 5

Polymerization of Cyclohexyl and Decahydro-2-Naphthyl Vinyl Ethers in Presence of Benzoyl Peroxide

Ether	Amt. of peroxide (%)	Yield (%)	Softening point (° C)	Mol. wt. of polymer	Appearance of polymer
Cyclohexyl vinyl	—	10,3	97—100	2595,00 2570,00	White solid obtained by boiling the ether for 5 hours
"	1,0	6,7	—	394,00	Colorless viscous; obtained by heating 140 hrs at 60°
"	5,0	53,6	—	572,7 582,6	Viscous, $\eta = 0.7079$, transparent
Decahydro-2-naphthyl vinyl	6,0	68,70	91—93	889,6 874,4	White solid

2. Polymerization of Decahydro-2-naphthyl and Cyclohexyl vinyl Ethers under the Action of Benzoyl Peroxide and Heat. A mixture of 0.1 mole of the vinyl ether and a corresponding amount of benzoyl peroxide was sealed in an ampoule and heated in a thermostat at 86° for five hours. No increase in viscosity was noted. The ampoules were left at room temperature for six weeks, after which the reaction mixture had become a very viscous colorless liquid. Precipitation and drying gave solid polymers, the characteristics of which were given in Table 5.

3. Copolymerization of Phenyl, Cyclohexyl, and Decahydro-2-naphthyl Vinyl Ethers with Methyl Acrylate and with Methyl Methacrylate in Presence of Benzoyl Peroxide. A mixture of 5 g of the ethers and 0.01 g (0.2%) of benzoyl peroxide was sealed in an ampoule, which was heated in a thermostat at 60° for 68 hours continuously.

The resulting copolymers were clear colorless products ranging from viscous liquids to solids. The copolymers were purified from monomers by two reprecipitations from acetone solution with methanol, and were dried at 60° (12 mm) to constant weight. The molecular weight was determined cryoscopically in benzene, the viscosity of a 1% benzene solution was determined with an Ostwald viscometer, and the softening point was determined in a thick-walled capillary. The yields and characteristics of the copolymers are shown in Table 6.

TABLE 6

Copolymerization of Vinyl Ethers With Methyl Acrylate and With Methyl Methacrylate

Ethers taken	Molar ratio of ethers	Yield of copolymer (% on original mixture)	Found in copolymer (%)		Ratio of monomers in copolymer (mole %)	Mol. wt. of copolymer	Softening point (°C)	Viscosity η_{sp} (centipoise)	Appearance of copolymer
			C	H					
Cyclohexyl vinyl ether and methyl methacrylate	1 : 3	80,0	62,84	8,19	14,3 : 85,7	3318	185—190	1,894	White, fibrous
	1 : 1	52,0	65,30	8,70	22,4 : 77,6	2736	190—195	1,715	Colorless solid
	3 : 1	26,0	65,75	9,12	30,6 : 69,4	2313	~180	1,200	White solid
Cyclohexyl vinyl ether and methyl acrylate	1 : 3	32,0	60,70	8,04	16,24 : 83,76	1790	95—100	1,149	Colorless solid
	1 : 1	25,0	63,9	8,66	31,2 : 69,8	2953	70—75	0,8414	"
	3 : 1	28,0	66,02	9,10	40,8 : 59,2	4124	75—80	0,8513	Clear colorless solid
Decahydro-2-naphthyl vinyl ether and methyl methacrylate	1 : 3	66,9	63,66	8,64	10,9 : 89,1	1798	192—200	1,512	White fibrous solid
	1 : 1	38,5	65,30	8,65	21,4 : 78,6	2283	180—189	1,242	White powder
	3 : 1	21,0	69,05	9,65	31,4 : 68,6	1943	150—158	0,9679	Light white powder
Decahydro-2-naphthyl vinyl ether and methyl acrylate	1 : 3	74,0	63,76	8,35	19,8 : 80,2	5007	—	0,9354	Colorless, rubbery
	1 : 1	42,0	68,67	9,13	36,0 : 64,0	1626	56—62	0,8202	Clear colorless solid
	3 : 1	22,00	70,79	9,42	44,0 : 56,0	2493	85—90	0,7738	White solid
Phenyl vinyl ether and methyl methacrylate	1 : 3	78,2	62,34	8,05	9,82 : 90,18	2818	250—257	2,113	White powder
	1 : 1	54,6	63,51	7,93	14,9 : 85,1	3213	240—250	2,100	White powder
Phenyl vinyl ether and methyl acrylate	1 : 3	54,0	60,70	7,10	15,4 : 84,6	3757	75—80	1,116	White rubbery solid
	1 : 1	45,3	63,30	8,25	24,4 : 75,6	2539	95—100	1,154	White solid
	3 : 1	41,0	65,09	6,92	30,9 : 69,1	3767	98—100	0,9763	"

SUMMARY

1. A study was made of the homo- and co-polymerization of cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl vinyl ethers by ionic and free-radical mechanisms.

2. Conditions were found for the preparation in good yield of polymers of cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl vinyl ethers and of their copolymers with ethyl, butyl, and phenyl vinyl ethers in presence of the BF_3-ether complex. Most of these polymers were solids.

3. The polymerization of cyclohexyl, decahydro-2-naphthyl, and 2-naphthyl vinyl ethers in presence of benzoyl peroxide or 2,2'-azobis[2-methylpropionitrile] requires a large amount (up to 6%) of initiator, the application of heat, and prolonged treatment, and the yields of polymers are low.

4. In presence of benzoyl peroxide, cyclohexyl, decahydro-2-naphthyl, and phenyl vinyl ethers can be brought into copolymerization with the methyl esters of acrylic and methacrylic acids; depending on the relative amounts of the monomers taken, copolymers of various compositions are formed with vinyl ether contents of up to 44%.

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RAMAN-SPECTRUM INVESTIGATION OF THE C–H BONDS OF CHLORO SILA- AND DISILA-HYDROCARBONS CONTAINING SILICON-ATTACHED CHLORINE AND THEIR CHLORO DERIVATIVES IN CONNECTION WITH PECULIARITIES OBSERVED IN THE CHLORINATION OF THESE COMPOUNDS*

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Radiation-induced chlorination of chloro(methyl)- and chloro(chloromethyl) silanes was carried out for the first time as recently as 1954 by Krieble and Elliot [2] and was later studied in special detail by Speier [3]. The chlorination of chloro(methyl)silanes was the subject of some other investigations [4]. Some phenomena were observed which, as Speier emphasized, have an essentially specific (anomalous) character when compared with the results of the chlorination of the corresponding carbon compounds; these were as follows. In chlorosilanes containing silicon-attached chloromethyl and methyl groups, the former are much more readily chlorinated than the latter, which is not observed in the corresponding carbon compounds.** Moreover, the tendency for the chlorination of the chloromethyl groups rather than the methyl groups in such silanes increases considerably as the number of chlorine atoms in the molecule increases:

$$\underset{B}{(CH_3)_2Si} - \underset{A}{CH_2Cl} \quad \text{chlorination in A} > \text{in B}$$

$$\underset{B}{(CH_3)_2Si(Cl)} - \underset{A}{CH_2Cl} \quad \text{chlorination in A} \gg \text{in B}$$

$$\underset{B}{CH_3Si(Cl_2)} - \underset{A}{CH_2Cl} \quad \text{chlorination in A} \ggg \text{in B}$$

The preferential character of the chlorination of the chloromethyl group in chloro(chloromethyl)methylsilanes is clearly illustrated by the comparison of two ratios of amounts of chlorination products of $(CH_3)_3XCl$ (X = C or Si), calculated from the data of Table 1:

$$\frac{(CH_3)_2C(Cl)CHCl_2}{(CH_3)C(Cl)(CH_2Cl)_2} = 0{,}67; \quad \frac{(CH_3)_2Si(Cl)(CHCl_2)}{(CH_3)Si(Cl)(CH_2Cl)_2} = 4{,}9.$$

* This paper is associated to a considerable extent with the contents of the paper [1].

** From the ratio of chlorination products obtained from $(CH_3)_3Si-CH_2Cl$, namely [3]:

$$\frac{(CH_3)_3SiCHCl_2}{(CH_3)_2Si(CH_2Cl)_2} = 0{,}66,$$

it might be concluded that no substantial preferential chlorination of the chloromethyl group is observed in this compound; such an inference has been made [5]. However, the following must be taken into account: in the compound $(CH_3)_3Si-CH_2Cl$ the number of C–H bonds in methyl groups is 4.5 times as high as the number of C–H bonds in chloromethyl groups and, in spite of this, the absolute number of chlorinated C–H bonds of chloromethyl groups is greater than the absolute number of chlorinated C–H bonds of methyl groups. In this case, therefore, the greater activity of chloromethyl groups in chlorination is quite evident.

TABLE 1

Distribution of Chlorination Products of $(CH_3)_3XCl$ (moles %) [3]

Formula of compound	X-C	X-Si
$(CH_3)_3XCl$	No data	41,5
$(CH_3)_2X(Cl)CH_2Cl$	8,4	39,0
$(CH_3)_2X(Cl)CHCl_2$	15,5	11,7
$(CH_3)_2X(Cl)CCl_3$	Traces	1,2
$(CH_3)X(Cl)(CH_2Cl)_2$	22,9	2,4
$X(Cl)(CH_2Cl)_3$	3,1	—
$CH_3X(Cl)(CH_2Cl)(CHCl_2)$	10,9	Traces

Another notable peculiarity of the chlorination of chloro(methyl)silanes is the great deactivation of the molecules of these compounds with respect to chlorination, which increases from compound (I) to compound (IV):

I. $(CH_3)_4Si$; II. $(CH_3)_3SiCl$; III. $(CH_3)_2SiCl_2$; IV. CH_3SiCl_3

It was found [3] that, for example, the rate of chlorination of $(CH_3)_3SiCl$ is nine times as high as that of $(CH_3)_2SiCl_2$. It must be emphasized, however, that when the chlorination of the compounds (I) – (IV) has started and chloromethyl groups have made their appearance, further chlorination proceeds rapidly. Thus, in the chlorination of CH_3SiCl_3 in the liquid phase [6] the intermediate chlorination products of this compound, i.e., $(CH_2Cl)SiCl_3$ and $(CHCl_2)SiCl_3$, could not be detected, but only the final chlorination product, $(CCl_3)SiCl_3$. However, as we have shown, the chloromethyl groups themselves are more and more deactivated with respect to chlorination as chlorine atoms accumulate on the silicon atom. Thus, in the chlorination of an equimolecular mixture of * $Cl_3Si(CH_2Cl)$ and $Cl_2Si(CH_3)(CH_2Cl)$ (Table 2), of the 50% of the first compound only 7,5% was chlorinated, and of the 50% of the second 42,5% was chlorinated. In other words, the compound in which the smaller number of chlorine atoms had been replaced by methyl groups $Cl_2Si(CH_3)(CH_2Cl)$ was indeed preferentially chlorinated; moreover, the chloromethyl group of this compound was preferentially chlorinated.

TABLE 2

Distribution of the Products of the Chlorination of a 1 : 1 Mixture of $Cl_3Si(CH_2Cl)$ and $Cl_2Si(CH_3)(CH_2Cl)$ (Percent of Total Amount of Mixture)

	Results of chlorination of components of the mixture	
	$Cl_3Si(CH_2Cl)$	$Cl_2Si(CH_3)(CH_2Cl)$
Taken for chlorination	50	50
Residue from chlorination	42,5	7,5
Chlorinated	7,5	42,5

For the explanation of these regularities in chlorination it is necessary to take account of various factors determined by the structures of the reacting molecules and the reaction conditions. Our task in the present investigation consisted solely in determining, with the aid of Raman spectra, how the state of the C – H bonds reacting with chlorine changes with change in the structure of the molecule and the presence of electronegative chlorine atoms.

EXPERIMENTAL

The spectra were determined with a Soviet ISP-51 three-prism spectrograph with a central camera; the exciting radiation was the mercury line at 4358 A. Before their spectra were determined all the substances were

* Chlorination of the mixture of $CH_3Si(Cl_2)CH_2Cl$ and Cl_3SiCH_2Cl. A mixture of 54.5 g (0.3 mole) of $CH_3Si(Cl_2)CH_2Cl$ (b. p. 121°) and 61.3 g (0.3 mole) of Cl_3SiCH_2Cl (b. p. 117°) was prepared in a flask fitted with reflux condenser, thermometer, and tube for the passage of chlorine. Chlorination was carried out at 100-105° for 57 hours under the radiation of a quartz lamp. The final boiling point of the mixture was 138°. Increase of weight 4.2 g. Fractionation through a column of 35-plate efficiency gave 45 g of a mixture (b. p. 117.5-119.5°) of unchanged reactants and 57.6 g of chlorination products. The latter were analyzed by the Raman-spectrum method. The results of the analysis are given in Table 2.

distilled twice through a 35-plate column. The second distillation was carried out directly into the vessel to be used in the spectrograph; precautions were taken against the entry of moisture. The physical properties of the compounds investigated are given in Table 3, and their spectra in Table 4.

TABLE 3

Physical Properties of Chloro(methyl)silanes, Chloro(chloromethyl)silanes, and Other Compounds

Compound No.	Formula of compound	B. p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR found	MR calculated
1	$Si(CH_3)_4$	25,5 (755)	0,6454	1,3634	30,37	30,28
2	$ClSi(CH_3)_3$	56,4	0,8586	1,3885	29,88	29,91
3	$Cl_2Si(CH_3)_2$	69,7(752,3)	1,0720	1,4038	29,44	29,54
4	Cl_3SiCH_3	65,5(745)	1,2630	1,4110	29,37	29,17
5	$Cl_3SiCH(Cl_2)$	143,5(747)	1,5518	1,4714	39,22	38,85
6	$Cl_3SiCH(Cl)SiCl_3$	211(755,5)	1,6521	1,4925	55,76	56,42
7	Cl_3SiCH_2Cl	117(752)	1,4646	1,4541	33,99	34,01
8	$Cl_3SiCH_2SiCl_3$	182,7(745)	1,5567	1,4740	51,58	51,13
9	$Cl_3SiCH_2CH_2SiCl_3$	201,5(726)	—	—	—	—
10	$Cl_3SiCH(Cl)CH_2SiCl_3$	226,2(746)	1,5887	1,4934	60,65	61,05
11	$CH_3Si(Cl_2)(CHCl_2)$	148(745,5)	1,4136	1,4700	39,07	39,22
12	$CH_3Si(Cl_2)(CH_2Cl)$	121(740)	1,2858	1,4500	34,98	34,38
13	$(CH_3)_2C(Cl)(CH_2Cl)$	105,6(752)	1,0950	1,4370	30,39	30,33
14	$(CH_3)_2Si(Cl)(CH_2Cl)$	114,3(752,5)	1,0862	1,4368	34,48	34,75
15	$(CH_3)_2CHSiH(Cl_2)$	96,5(741)	1,0696	1,4209	—	—
16	$(CH_3)_2CHSiCl_3$	119,3(745)	1,2024	1,4332	38,39	38,43
17	$(CH_3)_3Si(CH_2Cl)$	97,2(799)	0,8861	1,4179	35,00	35,12
18	$Cl_3SiCH_2CH_2CH_3$	122,5(729,5)	1,2028	1,4250	38,27	38,43
19	$Cl_2SiHCH_2CH_2CH_3$	101,5(747,5)	1,0655	1,4200	—	—

TABLE 4

Raman Spectra of Chloro(methyl)silanes, Chloro(chloromethyl)silanes, and Other Compounds

1. $Si(CH_3)_4 \cdot \Delta\nu\ cm^{-1}$: 201(5), 245(4), 595(10), 697(4), 863(4 дв, ш), 1265(2), 1421(3), 2899 (10ш), 2958(10 ш)

2. $ClSi(CH_3)_3 \cdot \Delta\nu\ cm^{-1}$: 187(7 ш), 239(6ш, дв), 469(7ш), 637(10р), 703(3ш), 762(4), 852(3ш), 1256(3), 1301(0), 1416(5), 2900(10), 2969(9ш)

3. $Cl_2Si(CH_3)_2 \cdot \Delta\nu cm^{-1}$: 177(7ш), 241(6ш, дв), 464(10), 533(3ш), 696(6), 805(3),842(0) 1265(2), 1393(4), 1409(2), 2907(10ш), 2977(9ш)

4. $Cl_3SiCH_3 \cdot \Delta\nu cm^{-1}$: 161(7ш), 230(6ш, дв.), 448(10), 570(4ш, дв, band), 762(5), 803(1дв), 1269(2), 1408(4), 2914(10), 2988(8ш)

5. $Cl_3SiCH(Cl_2) \cdot \Delta\nu cm^{-1}$: 114(5), 166(8), 196(4), 238(5), 264(3), 336(10), 468(10), 602(3*), 615(3*), 646(5), 740(5), 829(3), 1147(4), 1192(4), 1397(0), 1457(1), 2963(6)

6. $Cl_3SiCH(Cl)SiCl_3 \cdot \Delta\nu cm^{-1}$: 84(3*),112(3*), 121(3*), 159(3*), 176(1**), 191(5**),206 (1**), 330(10), 479(9), 594(4), 622(2), 648(3), 772(4), 791(0), 821(1), 1069(3), 1351(0),2896(4)

7. $Cl_3SiCH_2Cl \cdot \Delta\nu cm^{-1}$166(7),214(6),277(5),315(0),456(10),479(1),596(4ш,дв, band), 677(7), 801(5), 1103(3), 1190(2), 1389(5*), 1407(2*), 2761(2) 2935(10), 2987 (8)

8. $Cl_3SiCH_2SiCl_3 \cdot \Delta\nu cm^{-1}$: 120(7), 171(1)189(7*), 200(7*), 248(4), 309(9р), 465(10), 565(3*)—581(5*)—609(2*) (band), 698(4ш), 796 (3ш), 1087(3), 1344(4), 1371(1),2887(8), 2924(4).

9. $Cl_3SiCH_2CH_2SiCl_3 \cdot \Delta\nu cm^{-1}$: 101(5), 131(7), 165(3), 198(4*), 214(3*), 239(2), 299(7), 482(10), 569(3*) — 587(3*)— 601(3*) (band), 767(4), 993(3). 1210(0). 1270(5). 1406(4), 2894(10), 2929(4), (line 101 on end of background of wing of Raleigh line).

10. $Cl_3SiCH(Cl)CH_2SiCl_3 \cdot \Delta\nu cm^{-1}$: 72(2*), 106(3*), 115(3*), 135(6*), 172(4), 197(6), 225(3р), 266(3), 312(10), 361(3), 422(1), 455(1), 493(10), 578(4*), 592(4*), 615(1*), 638(5), 675(0), 733(2), 767(5), 799(1), 826(6), 891(2), 1006(4), 1154(4). 1222(5), 1256(0), 1289(6 р), 1320(0), 1353(0), 1390(4), 2888(6), 2917(5*), 2934(3*), (lines 73-135 on background of wing of Raleigh line)

(Continued)

TABLE 4 (Continued)

11. $CH_3Si(Cl_2)(CHCl_2)$ · Δνcm^{-1}: 117(2 ш. дв.), 145(2*), 168(5*), 186(5*), 208(3*), 243 (3ш. дв), 263(2*), 273(2*), 325(7p), 346(6 p), 477(6*), 493(7*), 567(3, band), 614(4), 722(4*), 744(3*), 786(2), 840(3), 1190(3*), 1222(2*), 1261(0), 1300(0), 1338(0), 1402 (3ш), 2908(10), 2950(3*),2972(6*), 2984(6*), (lines 117-208 on background of wing of Raleigh line)

12. $CH_3Si(Cl_2)(CH_2Cl)$ · Δν^{-1}cm^{-1}: 165(5), 187(5), 226(6), 270(5), 310(2), 474(10), 553 (3ш), 655(6), 695(2), 736(4), 771(2), 803(3), 827(3), 1105(3), 1189(2), 1234(0), 1263(1). 1398(4), 2910(10), 2937(9), 2984(9 ш).

13. $(CH_3)_2C(Cl)(CH_2Cl)$ · Δνcm^{-1}:195(1 ш), 212(1), 235(1), 277(4), 362(5), 420(4), 466(1), 522(1), 576(5ш), 626(5ш), 694(1), 726(6ш), 754(2ш), 815(5*)— 828(3*) (band), 938(0) 968(0), 1114(3),1155(0), 1239(0), 1276(2), 1384 (0), 1441(4**),1455(3**),2914 (3*), 2937(6*), 2964 (2**), 2984(m**), 3006(2**), (line 195 on end of background of wing of Raleigh line)

14. $(CH_3)_2Si(Cl)(CH_2Cl)$. Δν cm^{-1}: 123(2), 191(6ш), 233(5ш), 266(3), 299(2), 483 (6ш), 611(2*), 622(9*), 660(1**), 686(4**), 710(1**), 758(5), 800(1), 829(1), 859 (1), 1194(1), 1259(1), 1402(4 дв. ш), 2905(10*), 2939(3*), 2974(10**), 2989(2**)

15. $(CH_3)_2CHSiH(Cl)_2$ · Δνcm^{-1}: 151(3*), 173(2*), 183(5*), 286(5), 355(2), 397(2), 495(10p), 517(5 p), 567(4ш), 643(4), 673(2), 801(5ш), 881(5p), 1079(3), 1245(5), 1283(2), 1448(4), 1469(4), 2196 (9 band),2727(1), 2870(10* p), 2901(3*p), 2936(3*), 2964(8*дв), (Lines 151-183 on background of wing of Raleigh line)

16. $(CH_3)_2CHSiCl_3$ · Δνcm^{-1}: 128(6ш), 180(7), 211(5), 307(2*), 319(6*), 344(0), 413(6), 457(10), 572(3*)— 588(3*)— 603(3*) (band), 679(3ш), 880(5), 971(1),1005(1), 1071(3), 1203(2), 1244(5), 1277(1), 1450 (5*), 1468(4*), 2724(1), 2874(10*), 2910(3*), 2936 (5*), 2958(7*), 2972(3*), (lines 128-211 on background of wing of Raleigh line).

17. $(CH_3)_3Si(CH_2Cl)$ · Δνcm^{-1}: 203(7ш), 238(6ш), 289(5), 584(10), 644(4), 701(5), 743(6), 856(4ш, дв, band), 1108(3), 1175(1), 1261(2), 1399(4*), 1416 (4*), 2900(10**), 2933(4**), 2960(9** ш), 2974(9**)

18. $Cl_3SiCH_2CH_2CH_3$ · Δνcm^{-1} : 127(2), 169(6ш, band), 209(6*p), 232(3*ш), 287(2 ш), 318(2), 337(7), 458(6p), 478(8p), 566(3*), 581(3*), 594(3*), 681(2**), 698(2**), 757(3), 879(3*), 898(3*), 1032(4), 1070(3), 1206(5), 1246(2), 1303(3ш), 1342(2), 1390(4*), 1407(4*), 1454 (8 ш), 2863(1 дв), 2928(2), 2872(10*), 2910(5*), 2936(7*), 2968(6*), 2991(1*)

19. $Cl_3SiHCH_2CH_2CH_3$ · Δνcm^{-1}: 123 (1*), 173(6*), 184(5*), 240(2*ш), 268(4*p), 293 (2*, дв), 347(3), 396(4), 496(9*),511(6*), 561(3ш), 648(2*), 667(2*), 685(4*p), 714(1), 743(3), 781(3*), 802(4*), 832(3*) 847(3*), 882(3**), 899(3**), 1012(1), 1036,(4), 1071(3), 1207(4), 1245(2), 1304 (3ш), 1346(3), 1459(6ш), 2206(8, band), 2736(0), 2876(10*), 2914(5*), 2939(7*), 2971(4*), 2996(1*), (lines 123-293 on background of wing of Raleigh line).

The intensities are given on a ten-grade visual scale. Abbreviations: ш is broad line; p is sharp line; дв is double line; asterisks indicate lines on a background which is common to neighboring lines indicated by the same number of asterisks.

DISCUSSION OF RESULTS

As we have shown previously [1], the electronization of C—H bonds of methylene and methyl groups and the orienting effect of chlorosilyl groups increase in the series $(C_2H_5)_3SiCH_2CH_3 \rightarrow (C_2H_5)Si(Cl)CH_2CH_3 \rightarrow (C_2H_5)Si(Cl_2)$-$CH_2CH_3 \rightarrow Cl_3SiCH_2CH_3$, and there is particularly great increase in the electronization (increase in effective electron density [8]) of the C—H bonds of methylene groups, which is expressed in the positions of the vibration frequencies of these bonds, in the increase in their energies, and in the simultaneous reduction in their lengths.

In the chloro(methyl)silanes that we are considering, the alkyl chains consist of single methyl groups. Now, in tetraethylsilane $Si(C_2H_5)_4$, in contrast to the case of normal paraffins, the most electronized C—H bonds are those of the methylene groups adjacent to the central atom [1]; and in chloro(methyl)silanes we have methyl groups adjacent to the central atom, the C—H bonds of which are also found to be strongly electronized.* Actually, as the data of Table 5 shows, the electronization of the C—H bonds of the methyl groups of tetramethylsilane is considerably greater than that of the C—H bonds of the methylene and methyl groups of normal paraffins and the methyl groups of tetraethylsilane; it is close to the electronization of the C—H bonds of the methylene groups of tetraethylsilane, which are adjacent to the central silicon atom.

* For a discussion of the electronization and protonization of bonds see [8].

TABLE 5

Vibration Frequencies of C—H Bonds of the Methylene and Methyl Groups of Various Compounds

Compounds	Vibration frequencies (cm^{-1})									
Normal paraffins CH_2	2853	—	—	2908	—	—	—	—	—	—
CH_3	—	2879	—	—	—	2938	—	2967	—	—
$Si(C_2H_5)_4$ CH_2	—	—	—	2908	—	—	—	2968	—	—
CH_3	—	2879	—	—	—	2940	2955	—	—	—
$Cl_3Si(C_2H_5)$ CH_2	—	—	—	—	—	2931	—	—	—	2996
CH_3	—	—	2895	—	—	—	2946	—	2978	—
$Si(CH_3)_4$	—	—	2899	—	—	—	2958	—	—	—
$ClSi(CH_3)_3$	—	—	2900	—	—	—	—	2969	—	—
$Cl_2Si(CH_3)_2$	—	—	—	2907	—	—	—	—	2977	—
$Cl_3Si(CH_3)$	—	—	—	—	2914	—	—	—	—	2988

TABLE 6

Frequencies of C—H Bonds of Chloro(chloromethyl)silanes and Other Compounds (cm^{-1})

Compound No.	Compound	CH_3**			CH_2**		CH
1	Paraffins*	2879	2938	2967	2853	2908	2870
2	$(CH_3)_4Si$	2899	2958	—	—	—	—
3	$Cl_3SiCHCl_2$	—	—	—	—	—	2963
4	Cl_3SiCH_2Cl	—	—	—	2935	2987	—
5	$(CH_3)Si(Cl_2)(CHCl_2)$	2908	2950	2984	—	—	2972
6	$(CH_3)Si(Cl_2)(CH_2Cl)$	2910	—	2984***	2937	2984***	—
7	$(CH_3)Si(Cl)(CH_2Cl)$	2905	—	2974	2939	2989	—
7a	$(CH_3)_2C(Cl)(CH_2Cl)$	2914	2964	2984	2937	3006	—
8	$(CH_3)_2Si(CH_2Cl)$	2900	—	2960	2933	2974	—

* Normal paraffins in the case of CH_3 and CH_2, and branched paraffins in the case of CH.

** The first column contains symmetrical vibrations, and the second and third contain antisymmetrical.

*** Merging frequencies; the frequency of the C—H of the methyl group is somewhat lower, and the frequency of the C—H of the methylene group somewhat higher than the mean position given.

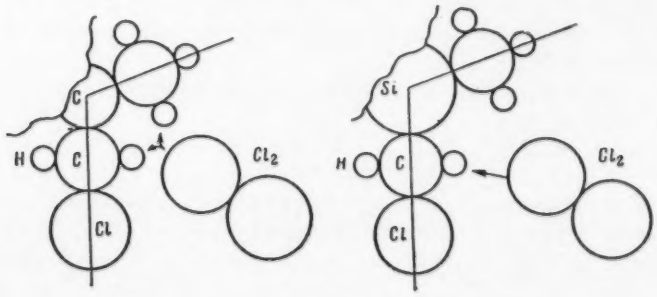
As the methyl groups of $(CH_3)_4Si$ are successively replaced by chlorine atoms, there is an increase in the electronization of the C—H bonds of the methyl groups which attains a maximum at $Cl_3Si(CH_3)$, just as in

chloro(ethyl)silanes the electronization of the C—H bonds of the methylene and methyl groups attains a maximum at $Cl_3Si(C_2H_5)$. As we have already seen [1], in the chloro(ethyl)silanes the accumulation of chlorine atoms on the central silicon atom results in an increase in the deflecting effect of the field of these atoms on an attacking chlorine molecule so that in $Cl_3SiC_2H_5$ the chlorination process is transferred from the α- to the β-position (and in chloro(propyl)silanes, further to the γ-position); and in the case of the chloro(methyl)silanes we have an analogous increase in the deflecting action of the field of the chlorine atoms as we pass from $Si(CH_3)_4$ to $Cl_3Si(CH_3)$. As however, the alkyl chain of chloro(methyl)silanes contains only one carbon atom, and not two or three as in the case of chloro(ethyl)- and chloro(propyl)silanes, this deflecting effect of the field of the chlorine atoms is naturally manifested in the chloro(methyl)silanes simply as a retardation of chlorination as we pass from $Si(CH_3)_4$ to $Cl_3Si(CH_3)$ and in the chloro(chloromethyl)silanes as the above-mentioned deactivation of the chloromethyl groups themselves. In this sense there is really no real anomaly in the chlorination of these compounds.

Let us now turn to the elucidation of the state of the C—H bonds of the chloromethyl groups of chloro-(chloromethyl)silanes, as compared with the state of the C—H bonds of the same groups in chloro(chloromethyl) methanes. Under the action of the chlorine atoms of the chloromethyl groups in these compounds there is an unusually sharp further increase in the electronization (not protonization) of the C—H bonds of methylene and methylidyne groups. This is confirmed by the data of Table 6. Actually, in Cl_3SiCH_2Cl and $Cl_3Si(CHCl_2)$, which contain one methylene group and one methylidyne group, respectively, the vibration frequencies of the C—H bonds of these groups exceed by more than 80-90 cm^{-1} the vibration frequencies of the C—H bonds of the methylene and methylidyne groups of paraffins, and greatly exceed also the vibration frequencies of the C—H bonds of both the paraffins and also the other compounds given in Table 6 (frequencies of symmetrical vibrations must be compared with frequencies of symmetrical vibrations and frequencies of antisymmetrical vibrations similarly with those of antisymmetrical vibrations). The significance of this exaltation is emphasized also by the fact that in the case of paraffins for example, the vibration frequencies of the C—H bonds of methylidyne and methylene groups lie substantially below those of the C—H bonds of methyl groups. In other compounds containing chloromethyl groups (Nos. 5-8, Table 6), the high electronization of the C—H bonds of methylidyne and methylene groups is maintained.

However, in the chloro(chloromethyl)methanes the C—H bonds of the chloromethyl groups are also electronized very greatly, as can be seen in the case of Compound No. 7a, Table 6. Hence, for the understanding of the differing behaviors of the chloromethyl groups of these compounds it is necessary to discover further factors determining the special activity with respect to chlorination shown by the chloromethyl groups of chloro(chloromethyl)silanes, when compared with chloro(chloromethyl)methanes or, on the other hand, discover circumstances leading to the extinction or masking of the activity of the chloromethyl groups of chloro(chloromethyl)methanes toward chlorination.

One such factor is clearly the difference in the spatial arrangement of the methyl and chloromethyl groups in these derivatives of silane and methane. As a result of the considerably greater dimensions of the silicon atom, the attached methyl and chloromethyl groups in chloro(chloromethyl)silanes are separated by a greater distance than in the corresponding carbon analogs, as shown in the figure. As a result, in the case of the chloro(chloromethyl)methanes, in which the chloromethyl and methyl groups are closer together, the probability for the attacking molecule, atom, or positive chlorine ion to collide with the C—H bonds of the neighboring methyl group becomes greater. It follows that, in the light of the above considerations and in spite of Speier's views [3], it is the chlorination of chloro(chloromethyl)methanes that is "anomalous," and not that of chloro(chloromethyl)silanes.



As regards the higher activity in chlorination of chloromethyl groups, as compared with methyl groups in the same molecule (e.g. in $CH_3Si(Cl_2)CH_2Cl$), apart from the factor of high electronization of the C—H bonds of methyl and methylene groups (Table 6) we must clearly take account also of the presence in the chloromethyl group of a polar C—Cl bond, which affects the orientation of chlorine molecules to this group; this must be supposed to occur also in molecules such as $Cl_3SiCH_2CH_2Cl$, $Cl_3SiCH(Cl)CH_3$, $C_4H_5CH_2Cl$, and $F_3CCH_2CH_2Cl$.

The conclusion that the accumulation of chlorine atoms both on silicon and in the alkyl chain leads to considerable increase in the electronization, i.e., to increase in the effective electron density [8], of the C—H bonds of this chain finds confirmation also in the case of various other organosilicon compounds, given in Table 7. In this paper we shall not discuss the relation of these changes to the peculiarities of their chlorination. We will mention only that the factors determining the direction of the chlorination process, its intensity, and its character (ionic, free-radical) lie in the chemical structures of the reacting molecules and the reaction conditions (catalysts, temperature, conditions of irradiation, etc.). The resulting effect of all these factors is dependent on their interrelationship: a particular structure in the molecule being attacked may have a substantial effect on, e.g., the degree of polarization of the attacking chlorine molecule and may direct the latter accordingly, and also in accordance with the geometry of the molecule being attacked, with the nature of its component atoms, with the polarization of its bonds, etc.; it may direct it also to a definite part of the molecule and deflect it from another, etc. Among all these factors an important part is clearly played in some cases by the degree of electronization of the bonds of the molecule being attacked,* a matter which has not received attention until recently.

TABLE 7

Frequencies of C—H Bonds of Some Organosilicon and Other Compounds

	Compound	Frequencies of bonds (cm^{-1})					
		CH_3**			CH_2**		CH
1	Paraffins*	2879	2938	2967	2853	2908	2870
2	$Si(CH_3)_4$	2899	2958		—	—	—
3	$Cl_3SiCH_2CH_3$	2895	2946	2978	2931	2996	—
4	$(CH_3)_2CHSiCl_3$	2874	2936	2972	—		2958
5	$Cl_3SiCH_2CH_2CH_3$	2872	2936	2968	—	—	—
	α-Position	—	—	—	2936	2991	—
	β-Position	—	—	—	2910	2965***	—
6	$Cl_3SiCH_2CH_2Cl$ [6]						
	α-Position	—	—	—	2940	3006	—
	β-Position	—	—	—	2912	2967	—
7	$Cl_3CCH_2CH_2Cl$ [6]						
	α-Position	—	—	—	2943	3020	—
	β-Position	—	—	—	2917	2977	—
8	$Cl_3SiCH_2SiCl_3$	—	—	—	2887	2929	—
9	$Cl_3SiCH(Cl)SiCl_3$	—	—	—	—	—	2896
10	$Cl_3SiCH_2CH_2SiCl_3$	—	—	—	2894	2928	—
11	$Cl_3SiCH(Cl)CH_2SiCl_3$	—	—	—	2888	2934	2917

* Normal paraffins in the case of CH_3 and CH_2, and branched paraffins in the case of CH.

** The first column contains symmetrical vibrations, and the second and third contain antisymmetrical [6].

*** Approximate position: frequency merges with background.

SUMMARY

1. As the number of chlorine atoms on the silicon and in the alkyl chains of alkylchlorosilanes increases there is a regular increase in the electronization (increase in effective electron density) of the corresponding C—H bonds.

* See [8], and also [1, 7].

2. Anomalies found in various investigations in the chlorination of chloro(methyl)- and chloro(chloromethyl)-silanes, as compared with the subsequent members of their homologous series and with their carbon analogs, were not confirmed. It should rather be considered that the course of the chlorination of chloro(chloromethyl)methanes is anomalous and that the anomaly is the result of complicating steric hindrance.

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BRIEF COMMUNICATIONS

SYNTHESIS OF ORGANOSILICON COMPOUNDS CONTAINING CHAINS OF PHENYLENESILOXANE GROUPINGS

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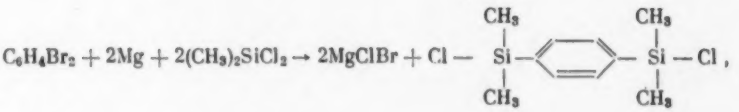
Organosilicon compounds in which there is a chain containing both phenylene and siloxane groupings are of considerable interest for study in comparison with polyorganosiloxanes. As is well known, polydimethylsiloxanes are highly elastic polymers in which the siloxane chains are very flexible. It is of interest to determine the effect of the introduction of benzene rings into the siloxane chain on thermostability and elasticity. We have begun an extensive investigation of the synthesis and properties of polymers containing chains of phenylenesiloxane groupings.

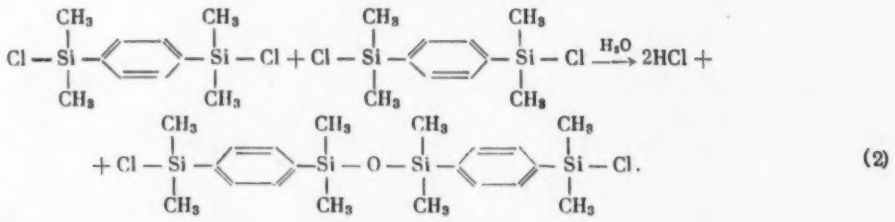
In the present paper we describe the first such compounds in which the siloxane units have methyl side groups; we prepared these by the action of magnesium on p-dibromobenzene with subsequent decomposition of the Grignard reagent with dichlorodimethylsilane. The experiments showed that reaction went according to the equation



(1)

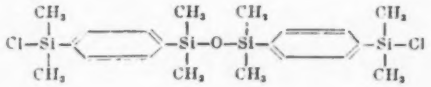
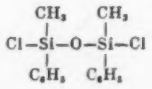
with formation of p-bis(chlorodimethylsilyl)benzene.

As a result of the high sensitivity of this substance to moisture, its yield was greatly reduced in the course of the separation of the solid products formed in the synthesis (ingress of moisture). At the same time there was a great increase in the amount of solid products. We made use of the high sensitivity of p-bis(chlorodimethylsilyl)benzene to hydrolysis for the preparation of condensation products containing chains of phenylenesiloxane groupings. For this purpose, in the separation of the liquid phase from the solid products we used moist ether in such quantity as to introduce 0.5 mole of water per mole of p-bis(chlorodimethylsilyl)benzene. By the use of this method we obtained phenylenesiloxanes. The reaction went as follows:

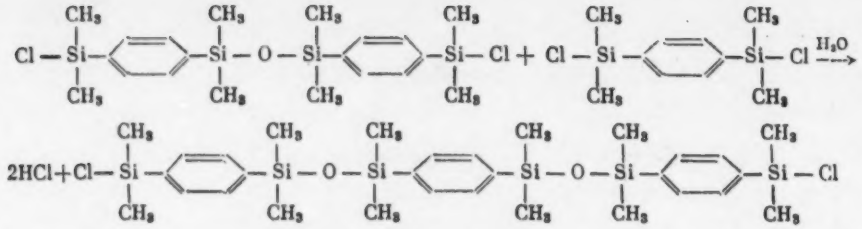


(2)

TABLE

Formula of compound	B.p. (° C) at 748 mm*	B.p. (° C) at p mm	d_4^{20}	n_D^{20}	MR found	MR calculated
	297	197—198 [1]	1,1089	1,5507	135,68	136,07
	365	—	1,0960	1,5522	198,34	198,79
	—	234—235 [2]	1,2147	1,5717	88,64	88,27

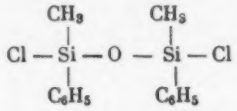
* The boiling point was determined by Sivolobov's method.



(3)

In the investigation of these reactions we isolated two condensation products of p-bis(chlorodimethylsilyl) benzene, (2) and (3). The properties of the new compounds are given in the table.

In the preparation of monomers for the synthesis of compounds containing chains of phenylsiloxane groupings with methyl side groups, we distilled some dichloromethylphenylsilane that had become moist and isolated the previously undescribed 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane



EXPERIMENTAL

1. Preparation of compounds containing phenylenesiloxane chains from p-bis(chlorodimethylsilyl)benzene. One mole (129 g) of dichlorodimethylsilane containing 55.80% Cl (calculated, 54.96% Cl) was added to $C_6H_4(MgBr)_2$ prepared from one mole (24.3 g) of magnesium and 0.5 mole (118 g) of p-dibromobenzene (m. p. 87.8°) in 400 ml of ether in presence of an iodine crystal. The mixture was boiled (42-45°) for six hours, and the solid magnesium compounds were washed with ether containing 4.5 g of water. Vacuum fractionation of the mixture gave 56 g (47.5%) of the substance (2), b. p. 197-198° (1 mm), and 3.7 g (3.3%) of the substance (3), b. p. 365°.

Found%: C 50.14; Si 23.34; Cl 14.96; H 6.71. $C_{20}H_{32}OSi_4Cl_2$. Calculated %: C 50.92; Si 23.82; Cl 15.03; H 6.84.

Mol. wt.: found 471; calculated 471.7

Found %: C 52.00; Si 24.05; Cl 10.37; H 7.32. $C_{30}H_{48}O_2Si_6Cl_2$. Calculated %: C 52.98; Si 24.78; Cl 10.42; H 7.11.

Mol. wt.: found 607; calculated 680.

2. Preparation of 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane. By the fractional distillation of 170 g of previously moistened dichloromethylphenylsilane we obtained 27.9 g (16.4%) of a substance of b. p. 234-235° (2 mm) corresponding in analysis to 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane.

Found %: C 51.61; C 21.96; Si 17.14; H 4.63. $C_{14}H_{16}OSi_2Cl_2$. Calculated %: C 51.36; Cl 21.66; Si 17.16; H 4.93.

SUMMARY

1. Two condensation products of p-bis(chlorodimethylsilyl)benzene were synthesized.

2. 1,3-Dichloro-1,3-dimethyl-1,3-diphenyldisiloxane was isolated.

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ACTION OF TRIALKYLALUMINUMS ON PHOSPHORUS TRICHLORIDE

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The reaction between trialkylaluminums and phosphorus trichloride has not been studied previously. Organolithium, organomagnesium, and organozinc compounds alkylate phosphorus trichloride to trialkylphosphines. By the action of organocadmium compounds (prepared via Grignard reagents) on phosphorus trichloride, low yields (26-43%) have been obtained of alkyldichlorophosphines [1]. Kharash [2] heated PCl_3 with tetraethyllead at 110° for 30 hours and obtained a 90% yield of dichloroethylphosphine. The action of dialkylmercurys [3, 4] on phosphorus trichloride gives difficultly separable mixtures of alkyldichloro- and dialkylchloro-phosphines with the original organomercury compound.

We found that, depending on the way in which the reaction was carried out, reaction between a trialkylaluminum and phosphorus trichloride leads to the formation of all three possible alkylated products from PCl_3:

$$AlR_3 + PCl_3 \rightarrow RPCl_2 + R_2PCl + R_3Al.$$

It was characteristic, however, that even in an excess of triethylaluminum, triethylphosphine is formed in a yield of only about 30%, and a considerable proportion of the Al—C bonds are preserved. In the reaction between equimolecular amounts of phosphorus trichloride and triisobutylaluminum the main product was chlorodiisobutylphosphine, which was identified in the form of diisobutylphosphinic acid. By reaction of trialkylaluminums with excess of PCl_3 we succeeded in obtaining satisfactory yields of alkyldichlorophosphines, which may be of definite interest in view of the accessibility of trialkylaluminums [5]. Since trialkyl- and dialkylchloro-phosphines give stable complexes with the aluminum halide compounds formed, only alkyldichlorophosphines distill from the reaction mixtures together with excess of PCl_3. Higher yields of alkyldichlorophosphines are attained when the trialkylaluminums are used as their complexes with ether or pyridine. In this way we prepared alkyldichlorophosphines $RPCl_2$, in which R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, and n-C_6H_{13}. Under the conditions of the reaction the alkyl groups did not undergo isomerization. We did not succeed in isolating dialkylchlorophosphines from the reaction mixtures, because they were bound as complexes with aluminum compounds; they can be isolated in the form of R_2POH or R_2POOH. We did not succeed in isolating dichloromethylphosphine from the products of the reaction of PCl_3 with the ether complex of trimethylaluminum.

EXPERIMENTAL

Dichloroethylphosphine. A solution of the "etherate" of triethylaluminum (prepared from 20 g of $(C_2H_5)_3Al$ and 25 ml of ether) was added in a stream of pure nitrogen with vigorous stirring to 110 ml of PCl_3 at 50-55° (attained as a result of the heat of reaction). A mixture of PCl_3 and $C_2H_5PCl_2$ was distilled off under reduced pressure (200 mm) into a cooled receiver. Fractionation through a 15-plate column gave 42.5 g (61.5%) of dichloroethylphosphine; b. p. 112°; $n^{25}D$ 1.4930; d^{20}_4 1.2600. The literature gives: b. p. 112°; $n^{25}D$ 1.4930; d^{27}_4 1.2485 [3]; d^{19} 1.2952 [3].

Dichloropropylphosphine. This was prepared similarly from 23 g of tripropylaluminum etherate and 55 ml of PCl_3; yield 22 g (50.6%); b. p. 133°; $n^{20}D$ 1.4860; d^{20}_4 1.1854. The literature gives: b. p. 134.5°; $n^{20}D$ 1.4842; d^{27}_4 1.1667 [1]; d^{19} 1.1771 [3]. Boiling of 10.7 g of n-$C_3H_7PCl_2$ with 2.4 g of sulfur in presence of 0.05 g of $AlCl_3$ for two hours gave 10.9 g of propylphosphonothioic dichloride; b. p. 62-63° (9 mm); $d^{20}D$ 1.5290; d^{20}_4 1.2832; found MR 42.42; calculated MR 42.43.

Found %: C 20.75, 20.75; H 4.20, 4.04; P 18.01, 17.73. n-$C_3H_7P(S)Cl_2$. Calculated %: C 20.36; H 3.96; P 17.50.

Propylphosphonothioic dianilide had m. p. 133° (from alcohol-water); m. p. of mixture with known sample [6] 132-133°.

Dichloroisopropylphosphine. Triisopropylaluminum (22.5 g) and 63 ml of PCl_3 gave 18.4 g (43.1%) of dichloroisopropylphosphine; b. p. 130° (745 mm); $n^{20}D$ 1.4880; d^{20}_4 1.1922. The literature [3] gives: b. p. 135-138°; d^{19} 1.2181.

Found %: Cl 49.05, 49.36. $i\text{-}C_3H_7PCl_2$. Calculated %: Cl 48.93.

From 7.2 g of dichloroisopropylphosphine and 1.8 g of sulfur we obtained 6.9 g of isopropylphosphonothioic dichloride; b. p. 63-64° (10 mm); $n^{20}D$ 1.5322; d^{20}_4 1.2956; found MR 42.36; calculated MR 42.43.

Found %: C 20.52, 20.52; H 3.96, 3.93; P 17.89, 17.40. $i\text{-}C_3H_7P(S)Cl_2$. Calculated %: C 20.36; H 3.96; P 17.50.

The dianilide had m. p. 114° (from benzene-heptane) and showed depression of melting point in admixture with $n\text{-}C_3H_7P(S)(HNC_6H_5)_2$.

Found %: C 62.10, 61.92; H 6.65, 6.43; S 11.30, 11.17; P 10.37, 10.57; N 9.59, 9.80. $i\text{-}C_3H_7P(S)(NHC_6H_5)_2$. Calculated %: C 62.04; H 6.60; S 11.04; P 10.67; N 9.65.

Dichloroisobutylphosphine. a) Triisobutylaluminum (32.5 g) was added to 120 ml of PCl_3 at 60-70°; in the vacuum distillation the excess of PCl_3 was followed by 11.5 g (17.6%) of dichloroisobutylphosphine; b. p. 59-60° (50 mm); 35-36° (9 mm); 148-149° (740 mm); $n^{20}D$ 1.4818; d^{20}_4 1.1268. The literature [3] gives: b. p. 155-157°; d^{23} 1.1236 [7]; b. p. 48.5-49.5° (12 mm); $n^{20}D$ 1.4719; d^{20}_4 1.172.

Found %: C 30.55, 30.67; H 5.75, 5.88; Cl 44.27, 44.72. $i\text{-}C_4H_9PCl_2$. Calculated %: C 30.21; H 5.64; Cl 44.60.

b) Triisobutylaluminum (94 g) in 50 ml of ether was added with vigorous stirring to 300 g of PCl_3 at 65-70°. By the procedure of the previous experiment we obtained 78.5 g (33%) of dichloroisobutylphosphine, b. p. 35-36° (9 mm); $n^{20}D$ 1.4822.

c) From 26.5 g of triisobutylaluminum in 11 ml of pyridine and 71 ml of PCl_3 we obtained 23 g (36 %) of dichloroisobutylphosphine.

Butyldichlorophosphine was prepared similarly to $n\text{-}C_3H_7PCl_2$ from 27.2 g of tributylaluminum etherate and 82.5 g of PCl_3; yield 27.4 g (57.4%); b. p. 153-155°, 38.5-39° (9 mm); $n^{20}D$ 1.4868; d^{20}_4 1.1416; d^{27}_4 1.1342. The literature [1] gives: b. p. 160°; $n^{25}D$ 1.4838; d^{27}_4 1.1341.

Dichlorohexylphosphine. Reaction between 38 g of trihexylaluminum and 80 ml of PCl_3 gave 32 g (42.5%) of dichlorohexylphosphine; b. p. 83-84° (9 mm); $n^{20}D$ 1.4820; d^{20}_4 1.0670. The literature [1] gives: b. p. 208°; $n^{25}D$ 1.4800; d^{27}_4 1.0653.

Triethylphosphine. Phosphorus trichloride (33.2 g) was added to 28.5 g of triethylaluminum; the mixture was heated (80°) with stirring for three hours. A viscous complex (60.5 g) was formed. Some of the complex (35.3 g) was decomposed with excess of aqueous sodium hydroxide, and triethylphosphine was extracted with ether. Fractionation in a stream of nitrogen gave 5.4 g (30%) of triethylphosphine; b. p. 129-130° and $n^{16}D$ 1.4575; the carbon disulfide adduct formed red needles, m. p. 121° (from alcohol). The literature [8] gives: b. p. 127.5°; $n^{18}D$ 1.45799; $(C_2H_5)_3PCS_2$, m. p. 121°.

Diisobutylphosphinic Acid. A solution of 23 g of phosphorus trichloride in an equal volume of heptane was added to 45 g of triisobutylaluminum in 50 ml of heptane (the temperature rose to 60-70° as a result of the heat of reaction). Heptane was vacuum-distilled from the complex formed, which was then decomposed with sodium hydroxide solution. The mixture of neutral and acid products was treated, with cooling, with 30% hydrogen peroxide, and diisobutylphosphinic acid was extracted with 20% sodium hydroxide solution; the alkaline solution was filtered from resinous impurities, washed with benzene, and acidified with hydrochloric acid. Benzene extracted 13.2 g of diisobutylphosphinic acid, b. p. 140-141° (0.4 mm) and m. p. 43-45° (from pentane). The literature [9] gives m. p. 41-44°.

Found %: C 53.40, 53.58; H 10.80, 10.59; P 17.36, 17.17. $(i\text{-}C_4H_9)_2PO_2H$. Calculated %: C 54.0; H 10.7; P 17.4.

SUMMARY

1. The reaction of trialkylaluminums with phosphorus trichloride was studied.

2. The conditions were worked out for the synthesis of alkyldichlorophosphines from phosphorus trichloride and the corresponding trialkylaluminums.

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HYDROGENOLYSIS OF BICYCLOPENTYL OVER A SKELETAL Ni – Al CATALYST

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It is known that the bicyclopentyl ring system undergoes isomerization with ring enlargement when hydriodic acid [1], zinc chloride [2], and phosphoric acid [3] react with 2-cyclopentylcyclopentanol. When bicyclopentyl was heated with aluminum chloride [3], cis- and trans-decahydronaphthalenes were found among the reaction products. Quite recently [4] we showed that at 450° in presence of hydrogen at a pressure of 20 atm bicyclopentyl isomerizes under the action of platinized alumina and zirconia into cis- and trans-decahydronaphthalenes, which are then dehydrogenated into tetrahydronaphthalene and naphthalene.

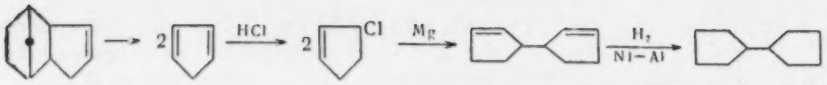
The hydrogenolysis of bicyclopentyl with the object of splitting off cyclopentane rings was studied by Eventova [5] under the conditions of dehydrogenation catalysis over platinized charcoal. On the basis of the physical properties of the fractions obtained from the catalyzate resulting from numerous passages of the bicyclopentyl, the author concluded that the reaction resulted in the formation of various paraffins and cyclopentanes, though no pure substances were isolated.

By the hydrogenolysis of cyclopentane homologs over a skeletal nickel-aluminum catalyst, we showed [6] that opening of the cyclopentane ring was accompanied by the formation of hydrocarbons with a carbon chain that had been shortened by the elimination of carbon atoms from the ring. It was suggested that the formation of these hydrocarbons proceeds by the "paired" cleavage of C–C bonds of the cyclopentane ring. In the present investigation, in order to determine the behavior of a five-membered ring in the hydrogenolysis of a bicyclic system we examined bicyclopentyl. We showed that at 200° only one ring of the bicyclopentyl undergoes cleavage, and the products are alkyl derivatives of cyclopentane.

EXPERIMENTAL

We synthesized bicyclopentyl as follows:

* Original Russian pagination. See C. B. Translation.



The product had the following properties: b. p. 189-189.5° (745 mm); $n^{20}D$ 1.4643 and d^{20}_4 0.8650. The hydrogenation of bicyclopentyl was carried out in an electric furnace by the flow method at 200° and at atmospheric pressure with a space velocity of 0.06 $hour^{-1}$ over a skeletal nickel-aluminum catalyst obtained by the removal of 15% of aluminum from an alloy of nickel (27%) and aluminum. In the experiment we took 61.2 g of the hydrocarbon. The yield of catalyzate was 72.7%. The catalyzate was fractionally distilled through a column of 70-plate efficiency. On the basis of the fractionation curve, narrow fractions were collected: these were characterized by their physical properties, and their compositions were determined from their Raman spectra. Chromathermographic analysis of the gas showed that it contained 71.1% of hydrogen, 23.4% of methane, 2.4% of ethane, 1.2% of propane, and 0.9% of butane.

The results of the fractionation of the catalyzate through a column are shown in the table.

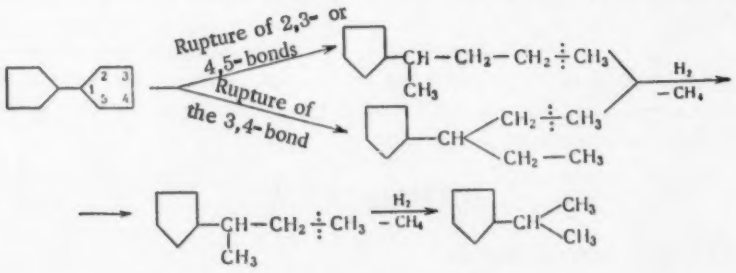
TABLE

Products of the Hydrogenolysis of Bicyclopentyl at 200° over an Ni—Al Catalyst

Fraction	B. p. (° C at 742 mm)	n^{20}_D	d^{20}_4	Yield (% on catalyzate)	MR found	MR calc.	Hydrogenolysis products
I	50—125,2	1,4080	0,7326	15,5	—	—	
II	125,2—125,4	1,4239	0,7717	6,0	36,94	37,02	Isopropylcyclopentane
III	125,4—151,2	1,4250	0,7732	10,5	—	—	
IV	151,2—152	1,4348	0,7939	12,4	41,47	41,36	sec-Butylcyclopentane
V	152—175	1,4350	0,7952	6,0	—	—	
VI	175—175,6	1,4403	0,8060	10,0	45,90	46,18	2- and 3-Cyclopentylpentanes
VII	175,6—188,6	1,4468	—	4,6	—	—	
VIII	188,6—189	1,4638	0,8645	16,4	44,09	43,98	Bicyclopentyl
Residue				2,4			

It will be seen from the table that, as in the case of cyclopentane homologs, bicyclopentyl undergoes cleavage with formation of not only 2- and 3-cyclopentylpentanes, but also hydrocarbons with a shortened alkyl chain, namely, sec-butylcyclopentane and isopropylcyclopentane.

Since appreciable dealkylation of side chains does not occur over skeletal nickel-aluminum [6], it is clear that the alkylcyclopentanes formed from bicyclopentyl must be demethylated before they are desorbed from the catalyst surface. It is here necessary to assume that in the hydrogenolysis one ring of bicyclopentyl is adsorbed on the catalyst surface in such a way that four CH_2 groups lie in one plane, whereas a CH group in the second ring remains raised above the catalyst surface. It is probable that a five-membered ring is first opened at one of the C—C bonds, and the alkylcyclopentane molecule then formed on the catalyst surface, without being desorbed, undergoes successive demethylations in the side chain with formation of hydrocarbons with a shortened side chain:



This mechanism does not preclude simultaneous cleavage at two C–C bonds of the cyclopentane ring on the catalyst surface. The results are confirmed also by the analysis of the gas. The proposed mechanism of the hydrogenolysis of bicyclopentyl is in accord with the results of Aston [7] and Kilpatrick [8].

SUMMARY

1. An investigation was made of the hydrogenolysis of bicyclopentyl over a skeletal nickel-aluminum catalyst at 200° at atmospheric pressure.

2. Under these conditions only one of the cyclopentane rings was hydrogenolyzed; this resulted in the formation of products of the simple rupture of C–C bonds of the ring and also of alkylcyclopentanes with a shortened side chain.

3. A scheme is proposed for the mechanism of the hydrogenolysis of bicyclopentyl.

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NOTE ON GLAUBERMAN AND IUKHNOVSKII'S EQUATION

Iu. M. Kessler and A. I. Gorbanev

Glauberman and Iukhnovskii's equation [1] for the electrostatic contribution to the free energy of an electrolyte solution has the form:

$$F_e = -(T/2D_0)\,\Sigma N_i z_i^2 \varepsilon^2 (B_1/2\beta^3\varkappa^2 T), \qquad (1)$$

in which $B_1 = \frac{1}{5}(x_1-1)^5 - \frac{2}{3}(x_1-1)^3 + (x_1-1) + \frac{1}{20}(x_1-2)^5 + \frac{1}{4}(x_1-2)^4 x_1$; $x_1 = \sqrt{1+2\beta\varkappa}+1$; β is a parameter of the theory (the mean diameter of the ions), and the remaining symbols have their usual meanings. Substituting $N_i = \nu_i N_2$ and $\varkappa^2 = AN_2$ in equation (1) (N_2 is the number of electrolyte molecules) and eliminating N_2 by cancellation, we obtain

$$F_e = -(T/2D_0)\,\Sigma\nu_i z_i^2 \varepsilon^2 (B_1/2\beta^3 AT). \qquad (2)$$

* Original Russian pagination. See C. B. Translation.

When $N_2 = 0$ (i.e., $\kappa = 0$), $B_1 \neq 0$, and therefore $F_e \neq 0$.

Equation (1) was obtained [1] by integration of the known thermodynamic equation (3), in which $\bar{U}_N$ is the mean potential energy of the interaction of the ions:

$$F_e = -T \int (\bar{U}_N / T^2)\, dT \tag{3}$$

As Glauberman and Iukhnovskii's expression for $\bar{U}_N$ gives $\bar{U}_N = 0$ when $\kappa = 0$, the incorrectness of equation (1) is probably due to a misprint or an error in the integration of (3). We therefore repeated the integration of (3), using the expression for $\bar{U}_N$ given by the authors of [1].

After the substitution of $\bar{U}_N$ and rearrangement, Equation (3) becomes

$$F_e = (T / 2D_0) \Sigma N_i z_i^2 \varepsilon^2 (I_1 - I_2), \tag{4}$$

in which

$$I_1 = \int (\kappa / T^2 \sqrt{1 + 2\beta\kappa})\, dT, \tag{5}$$

$$I_2 = \int [\kappa^2 / T^2 \sqrt{1 + 2\beta\kappa}\, (\kappa + 1 / \beta + \sqrt{1 + 2\beta\kappa} / \beta)]\, dT \tag{6}$$

Equations (5) and (6) are readily integrated with the aid of the substitution $x = \sqrt{1 + 2\beta\kappa}$. We obtain

$$I_1 - I_2 = B / 2\beta^3 \kappa^2 T, \tag{7}$$

in which $B = x(x-2) + 2x^3/3 - x^4/2 + C$; and C is the integration constant. Substituting (7) in (4) and applying the limiting condition of $F_e = 0$ at $\kappa = 0$, which gives $C = 5/6$, we finally obtain

$$F_e = (T / 2D_0) \Sigma \nu_i z_i^2 \varepsilon^2 (B / 2\beta^3 AT). \tag{8}$$

In the application of equation (1) for the calculation of heats of dilution ΔW it was found that $\Delta W_{(1)} = -\infty$ when $\kappa = 0$. Equation (8) gives the indefinite expression $\Delta W_{(8)} = 0/0$ when $\kappa = 0$, but investigation of this indeterminancy showed that $\lim \Delta W_{(8)} = 0$ for $\kappa \rightarrow 0$, so that equation (8) can be regarded as correct. The equation for $\Delta W_{(8)}$ satisfactorily describes experimental data for aqueous solutions of 1:1 electrolytes at 25° with β = about 4A and $\partial\beta / \partial T$ = about $5 \cdot 10^{-4}$ A/degree.

SUMMARY

An error in Glauberman and Iukhnovskii's equation was corrected.

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SYNTHESIS OF SILICON-CONTAINING ACETYLENIC ALCOHOLS

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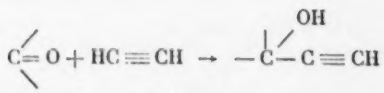
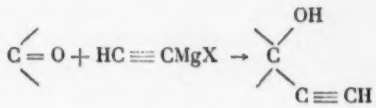
As is well known, acetylenic alcohols can be synthesized either by the condensation of ketones with acetylene in presence of KOH:



(1)

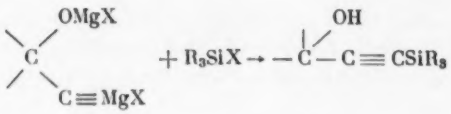
or by their reaction with a Grignard reagent prepared by Iotsich's method:



(2)

The yields obtained by reaction (2) are very low because of the low yields of Grignard reagent, and it is only recently, as a result of the work of Jones [1] and Normant [2], that it has been possible to improve them by the replacement of diethyl ether by tetrahydrofuran.

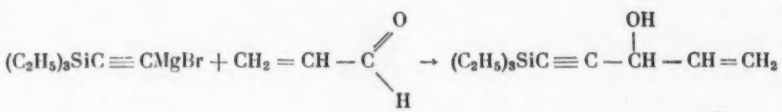
We have previously [3] prepared tertiary acetylenic alcohols by the reaction:



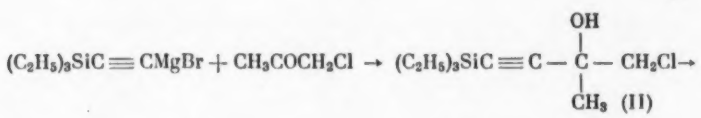
In the present investigation we showed that in tetrahydrofuran the reaction

$$HC\equiv CMgX + R_3SiX \rightarrow R_3SiC\equiv CH + MgX_2$$

gives high yields of triethylethynylsilane, and we used the Grignard reagent from this acetylenic silahydrocarbon for the synthesis of some alcohols and other compounds:



(I)



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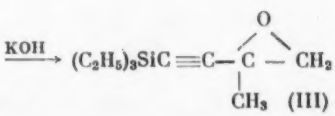

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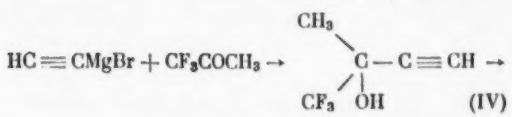

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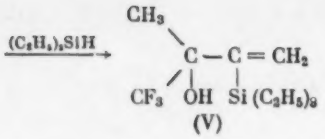


(V)

$$(C_2H_5)_3SiC \equiv CMgBr + CO_2 \rightarrow (C_2H_5)_3SiC \equiv C - COOH$$

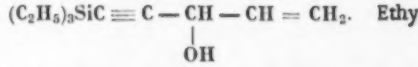
It was necessary to apply heat to bring about addition of bromine to triethylethynylsilane, and even prolonged boiling with excess of bromine in CCl_4 resulted only in the formation of the dibromide. Unlike the analogous compound in which fluorine was absent, the unsaturated alcohol (V) was not dehydrated by $KHSO_4$.

(Triethylsilyl)propiolic acid was dissolved in ether and precipitated on the walls of the beaker in the form of long needles, which were washed on the filter with octane. Distillation of this acid (a β-silyl carboxylic acid) resulted in its decomposition; it was also not found possible to determine its melting point. The infrared spectrum of the crystals was investigated in the region 700-4000 cm^{-1} (with LiF and NaCl prisms); ν (cm^{-1}): ~ 3299 (med) ~ 3167 (med), 2960 (str.), 2939 (str.), 2915 (str.), 2881 (str.), 2811 (weak), 2739 (weak), ~ 2070 (weak), 1610 (v. wk.), 1464 (med), 1392 (v. wk.), 1338 (str.), 1235 (med), 1012 (str.), 970 (med), 952 (str.), 918 (weak), 785 (med.) 730 (str.).

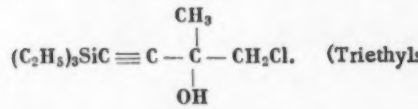
The presence of the carboxy group was characterized by the frequencies 3299, 3167, and 1640 cm^{-1}. The value of the vibration frequency of the C ≡ C bond (2070 cm^{-1}) is in accord with the value of the frequency of this bond in $(C_2H_5)_3SiC \equiv CH$ (2030 cm^{-1} in the Raman spectrum and 2050 cm^{-1} in the infrared spectrum).

EXPERIMENTAL

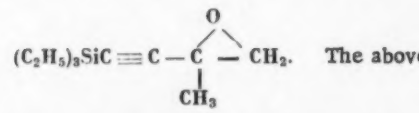
$(C_2H_5)_3SiC \equiv CH$. Ethynylmagnesium bromide was prepared by Jones's procedure from 11.5 g of magnesium, 55.0 g of ethyl bromide, and acetylene in 300 ml of dry tetrahydrofuran, and 71.0 g of bromotriethylsilane was added. The contents of the flask were stirred for six hours at room temperature and decomposed with saturated ammonium chloride solution.



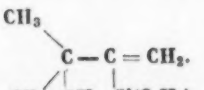
. Ethynylmagnesium bromide was prepared from 2.0 g of magnesium and 12.0 g of ethyl bromide in dry ether; 12.0 g of triethylethynylsilane was added dropwise, and the contents of the flask were boiled for three hours. The resulting complex was cooled with ice while 6.0 g of freshly distilled acrolein was added. On the next day decomposition was effected with acidified water, the ether layer was separated and dried, ether was distilled off, and the residue was fractionated.



. (Triethylsilyl)ethynylmagnesium bromide was prepared from 2.0 g of magnesium, 12.0 g of ethyl bromide, and 12.0 g of triethylethynylsilane in dry ether. The mixture was cooled with ice while 10.0 g of chloroacetone was added.



. The above chlorohydrin (7.2 g) was dissolved in 50 ml of dry ether in a flask fitted with reflux condenser, and with shaking 6.0 g of KOH powder was added gradually. Test for halogen was negative. The precipitate was then filtered off, ether was distilled from the filtrate and the residue was fractionated.



. Trifluoroacetone was prepared from trifluoroacetic acid in dibutyl ether. The tri-

TABLE

Formula of compound	B. p. in °C (p in mm)	M.p. (°C)	n_D^{20}	d_4^{20}	MR found	MR calc.	Yield (%)	Found % C	Found % H	Found % Si	Found % Cl	Calculated % C	Calculated % H	Calculated % Si	Calculated % Cl
$(C_2H_5)_3SiC{\equiv}CH$	138,0—138,5 (771)	—	1,4302	0,7862	46,03	46,65	85	68,51	11,42	20,05	—	68,48	11,49	20,02	—
$(C_2H_5)_3SiC{\equiv}C{-}CH(OH){-}CH{=}CH_2$	129,8—130 (15)	—	1,4708	0,8858	61,93	62,16	60	67,52	10,26	14,29	—	67,28	10,26	14,30	—
$(C_2H_5)_3SiC{\equiv}C{-}C(OH)(CH_3){-}CH_2Cl$	122 (5)	—	1,4725	0,9663	67,43	67,47	60	56,56	9,09	11,74	15,37	56,73	9,09	12,06	15,24
$(C_2H_5)_3SiC{\equiv}C{-}C(O){-}CH_3$ CH_3	99,5—100,5 (6)	—	1,4580	0,8775	60,93	60,72	82	67,40	10,19	14,21	—	67,28	10,26	14,30	—
$(C_2H_5)_3SiCBr{=}CHBr$	126,5 (10)	—	1,5180	1,4249	63,82	63,69	—	32,44	5,57	9,96	—	32,01	5,37	9,36	—
$CH_3{>}C(CF_3)(OH){-}C{\equiv}C{-}CH_3$ $Si(C_2H_5)_3$	114—115 (22)	—	1,4291	1,0342	63,42	63,86	—	51,94	7,98	—	—	51,93	8,30	—	—
$(C_2H_5)_3SiC{\equiv}C{-}OOOH$	—	Decomp.	—	—	—	—	—	—	—	—	—	58,64	8,75	15,24	—

fluoroacetone was distilled over phosphoric oxide into cooled ethynylmagnesium bromide. After the usual treatment and drying, two fractionations gave a product of b. p. 101-102.5°, $n^{20}D$ 1.3720 and d^{20}_4 1.1277.

A mixture of 9.0 g of the resulting alcohol and 0.25 ml of 0.12 N H_2PtCl_6 in isopropyl alcohol was placed in a flask fitted with reflux condenser and was heated while 9.0 g of triethylsilane was added gradually.

SUMMARY

1. Some derivatives of triethylethynylsilane were synthesized from its Grignard reagent, which was prepared in tetrahydrofuran in high yield.

2. By the addition of triethylsilane to 1,1,1-trifluoro-2-methyl-3-buten-2-ol the silicon- and fluorine-containing tertiary unsaturated alcohol 1,1,1-trifluoro-2-methyl-3-(triethylsilyl)-3-buten-2-ol was obtained.

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[2] H. Normant and T. Guvigny, Bull. Soc. Chim. France 447 (1957).

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Institute of Silicate Chemistry of the
Academy of Sciences of the USSR

Received March 11, 1958

* Original Russian pagination. See C. B. Translation.

LETTERS TO THE EDITOR

1-BUTANEBORONIC DIFLUORIDE: A POLYMERIZATION CATALYST

In collaboration with Fedorova, one of us has shown [1] that the addition of boron trifluoride "etherate" to tributylborine greatly increases the catalytic activity of the latter in the polymerization of acrylonitrile. This increase in catalytic activity may be the result of the formation of tributylborinic fluoride and 1-butaneboronic difluoride, and the polymerization catalyst may be one or both of these acid fluorides. With the object of verifying this suggestion we synthesized 1-butaneboronic difluoride [2] and carried out the polymerization of acrylonitrile in xylene in presence of this compound. It was found that, other conditions being equal, the yield of polyacrylonitrile in presence of 1-butaneboronic difluoride was 31.2%, whereas that in presence of tributylborine was only 5.3%. It was shown that 1-butaneboronic difluoride is a catalyst also for the polymerization of methyl methacrylate and styrene, the yields of polymers at a catalyst concentration of 0.2 mole percent being 95% and 89%, respectively.

Hence, it may be regarded as experimentally established that 1-butaneboronic difluoride is a catalyst for the polymerization of unsaturated compounds.

G. S. Kolesnikov and T. I. Ermolaeva

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Institute of Heteroorganic Compounds of the
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Received April 26, 1958

CARBOHYDRATE-PEPTIDE COMPLEXES

We have investigated the addition of peptides to carbohydrates with formation of carbohydrate-peptide complexes. We carried out the copolycondensation of anhydrides of N-carboxy derivatives of glycine and DL-alanine in an aqueous-dioxane medium at 0-1° with water-soluble carboxymethylcellulose having a degree of substitution of 75-80%. The products gave colored copper "biuret" complexes and a positive reaction for carbohydrates. As the degree of polymerization increased the carbohydrate-peptide complex changed its solubility in water; it contained 0.22-0.35% of amine nitrogen.

By conversion of the carboxy groups of the carboxymethylcellulose into mixed anhydride groupings by reaction with chloroformic ester and condensation of the product with DL-alanylglycine and with tetra-DL-alanine

* Original Russian pagination. See C. B. Translation.

we obtained water-soluble carbohydrate-peptide compounds giving the corresponding colored copper "biuret" complexes and a positive reaction for carbohydrates. We obtained other products by the copolycondensation of the anhydrides of the N-carboxy derivatives of glycine and DL-alanine with methyl glucoside and with xylose.

K. T. Poroshin

N. D. Zelinskii Institute of Organic Chemistry of the
Academy of Sciences of the USSR

Received May 29, 1958

CURRENT EVENTS

OLEG ALEKSANDROVICH ALEKIN

(In honor of his fiftieth birthday)

In August, 1958, Oleg Aleksandrovich Alekin, Doctor of Geographical Sciences and Corresponding Member of the Academy of Sciences of the USSR, attained the age of 50.

For about thirty years O. A. Alekin has worked in the field of hydrochemistry. While still a student at the Leningrad State University he entered the State Hydrological Institute, and in the course of his 22 years at this institute he worked his way from laboratory worker to the post of head of the hydrochemical section of the institute.

In his study of the chemistry of natural waters from various sources (lakes, underground waters, and rivers), Alekin directed systematic hydrochemical researches at the hydrological stations of the Hydrometeorological Service; he developed and published methods of work in hydrochemical investigations. The largest of his manuals, "Guide to the Chemical Analysis of Inland Waters," published in 1941 and reissued in 1952, is still used as the basis of the work of the whole hydrological network of the Hydrometeorological Service of the USSR.

On the basis of material gathered in the course of field investigations (Alekin took part personally in ten major expeditions) and also of the mass observations of the Hydrometeorological Network, Alekin worked out a hydrochemical classification of rivers as the necessary basis for the treatment of mass analyses. The fundamental principle of this classification is the coupling of the proportions of ions with their prevailing contents in natural waters.

All Alekin's researches are guided by the general idea of the further development of hydrochemistry, this young branch of knowledge. Thus, his hydrochemical classification of rivers was essential for his subsequent researches on the generalization of information on the chemistry of natural waters. These generalizations resulted in the publication of his monograph "General Hydrochemistry" in 1948. This monograph treats the hydrochemical peculiarities of various water systems (rivers, lakes, seas, and underground waters) as the result of mutually associated chemical processes occurring therein but modified by the respective concrete conditions peculiar to the different kinds of water systems. "General Hydrochemistry" is the first work of its kind in the whole of world literature; it gives the definition of the science of hydrochemistry and it generalizes the whole of our knowledge of the chemistry of natural waters. It is not surprising, therefore, that it serves as a reference book for all who study hydrochemistry and is the main textbook approved by the Ministry of Higher Education for use in universities. The fact that this work has originated in the USSR is a direct proof of the priority of Soviet science in the study of natural waters.

As soon as he had completed this important work, Alekin turned to other scientific projects; he wrote the large monograph "Hydrochemistry of the Rivers of the USSR" (1948-1949), which was based on researches by the author over many years on extensive hydrochemical material collected by the hydrological network of the Hydrometeorological Service of the USSR from 1938 onward. In his monograph, on the basis of 20,000 analyses about 1300 rivers of the whole territory of the USSR are characterized in their relation to the individual river basins, the information on the chemistry of which was confined to a few isolated data before the appearance of Alekin's book. Nothing resembling this treatise in size, in the extent of the territory covered, and in the profundity of the generalizations has yet appeared in the USSR or in any other country. An important result which emerges from

this work is the zonality that Alekin established for the chemical composition of river water over the territory of the USSR, this being based on the very close relation between the chemical composition of the water and the geographical medium. This zonality appears not only in the extent of mineralization, but in the proportions of the ions. The material presented in this book is now widely used by various planning, manufacturing, and scientific organizations. The monograph "Hydrochemistry of the Rivers of the USSR" was regarded as highly important, and in 1951 it was awarded a Stalin prize (Section of Chemical Science).

In October 1951, by a decree of the general membership and the Presidium of the Academy of Sciences of the USSR, O. A. Alekin was appointed as Director of the Hydrochemical Institute of the Academy of Sciences of the USSR with the object of strengthening the administration of the institute. In this capacity Alekin reorganized the research work so as to bring it closer to the demands of our national economy. As a result of his efforts and great energy, new laboratories have been added to the institute and the staff has been increased more than two-fold. The laboratories are equipped with modern apparatus and instruments. As a result of these measures the institute has been able to carry out some important investigations very expeditiously under Alekin's direction; these include the study of the hydrochemical regime of the Tsimliansk reservoir, a prognosis of the mineralization of the waters of the Main Turkmen Canel, a study of the Amu-Dar'ya River and of the ponds of the arid districts of European USSR, and a prognosis of the change in the composition of the water of Lake Balkhash which will result from the control of the waters of the River Ili. During the same period he wrote several monographs: "Hydrochemistry," "Course of Hydrochemistry," "Chemical Analyses of Inland Waters," several articles on carbonate equilibrium in natural waters, and various other works.

O. A. Alekin has published more than eighty scientific papers. The investigations described have brought us to an important stage in the evolution of the science and chemistry of natural waters and have created a new line of work, which in our country is led by O. A. Alekin. In 1953, Alekin was elected as a Corresponding Member of the Academy of Sciences of the USSR.

Alekin's work is widely known abroad. His main works have been published in Poland, China, Rumania, and Germany. In addition to his research work, Alekin has carried out teaching duties. From 1939 to 1941, and later from 1949 to 1951, he gave a course of hydrochemistry in Leningrad University; in 1943-1945 he gave courses of general chemistry in Archangel Medical Institute; and in 1951 he held an additional appointment as director of the Department of General and Analytical Chemistry in Leningrad Institute of Pediatric Medicine. From 1955 to 1957 Alekin combined his main work in the Hydrochemical Institute with the position of Rector of Rostov University. Apart from this, for several years Alekin directed the preparation of doctrants and aspirants.

Being a true son of the Communist Party of the Soviet Union, Alekin did a large amount of public work. In the Hydrological Institute he was on several occasions elected as member of the Bureau and as Assistant Secretary of the Party Organization. For several years he was a member of the Rostov District and City Committees of the Communist Party of the Soviet Union. He was elected to the Soviet of Deputies of the Workers for Rostov and also for Novocherkassk. He was a delegate at the historic Twentieth Congress of the Communist Party of the Soviet Union. As a participant in the Great Patriotic War, Alekin was severely wounded in battle in the breaking of the blockade of Leningrad, and he was awarded orders and medals of the Soviet Union.

O. A. Alekin is at the height of his creative efforts and continues to work fruitfully in the field of hydrochemistry. We wish him many more years of life, health, and successful work for the welfare of Soviet science.

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCE OF THE ACADEMY OF SCIENCES OF THE USSR, APRIL 24-25, 1958

An ordinary General Meeting of the Division of Chemical Science of the Academy of Sciences of the USSR was held on April 24-25, 1958, and papers were read by Corresponding Members of the Academy A. A. Grinberg, I. A. Kazarnovskii, and A. D. Petrov, and by Doctor of Chemical Science R. Kh. Freidlina.

A. A. Grinberg reported new information on the kinetics and mechanism of exchange and substitution reactions of complex platinum compounds. On the basis of experimental data obtained at the V. I. Khlopin Radium Institute in collaboration with S. S. Borzakovskii, E. N. In'kova, N. V. Kiseleva, G. A. Shagisultanova, and Iu. N. Kukushkin the author was able to make some interesting generalizations. By the extension of the investigations on isotopic exchange in complex platinum compounds to complex ions with neutral ligands (thiourea, ethylamine) it was shown that complex platinum compounds include both "labile" and "inert" complexes; on the basis of this A. A. Grinberg concluded that Taube's theory, which relates the lability or inertness of a complex with the structure of the electron shell of the central atom, is not applicable to bivalent platinum derivatives.

As a result of an investigation of the behavior of PdX_4^{--} and PtX_4^{--} ions in aqueous solution by various methods it was shown that the rate of the reversible hydration and the position of the equilibrium depend on the nature of the ligand in a definite way.

On the basis of experimental data A. A. Grinberg concludes that both dissociation and association mechanisms can play important parts in the isotopic-exchange processes of bivalent palladium derivatives. In the case of bivalent platinum derivatives the main role is played by the dissociation (hydration) mechanism, under the conditions studied. A. A. Grinberg reported the results of an investigation of the kinetics of the reaction of various complex ions of bivalent platinum with caustic alkali, ammonia, and pyridine. A comparison of the results showed that for bivalent platinum derivatives there is a cis effect in some cases as well as a trans effect. A discussion was given of the relation between the cis and trans effects in quadrivalent platinum compounds.

The paper was received with great interest and prompted a lively discussion, in which the following participated: Academician I. I. Cherniaev, Corresponding Members of the Academy V. I. Spitsin, Ia. K. Syrkin, and I. V. Tananaev, Doctor of Chemical Science A. D. Gelman, and others.

I. A. Kazarnovskii reported the results of an investigation, carried out in collaboration with S. I. Reikhshtein and L. N. Bykova, on the kinetics and mechanism of the spontaneous decomposition of potassium ozonide; they used the magnetic method.

At room temperature potassium ozonide slowly yields oxygen according to the equation $2KO_3 = 2KO_2 + O_2 + 11.6$ kcal. Study of the kinetics of this reaction revealed its autocatalytic character and the existence of an induction period. Measurements of magnetic susceptibility made at 20° and 0° simultaneously with the kinetic measurements indicated intermediate formation of atomic oxygen; this was confirmed by the observed formation of traces of ozone. It was found that at the start of the decomposition the content of atomic oxygen in the solid reaction mixture increases, passes through a maximum when the potassium ozonide is decomposed to an extent of about 50%, and then falls to zero. At the maximum point the solid phase contains about 20% of the whole of the oxygen produced in the form of atoms. In the graphs for the rate of formation of atomic oxygen against time, as also in the graphs for the rate of liberation of molecular oxygen against time, there are very marked topochemical maxima corresponding to a degree of decomposition of about 50%. The results support the hypothesis that the induction period is determined by an accumulation of defects in the potassium ozonide lattice, i.e., O_2^- ions and oxygen atoms; when a certain critical number of these defects is attained, the original structure breaks down into a phase saturated with defects and nuclei of a new phase, KO_2. This moment corresponds to the start of the active period of reaction, which then proceeds preferentially at the interface of the two phases.

Speaking on behalf of a group of workers at the Institute of Organic Chemistry (V. F. Mironov, V. A. Ponomarenko, S. I. Sadykh-Zade, and E. A. Chernyshev), A. D. Petrov read a paper entitled "Synthesis of New Kinds of Silicon-containing Monomers". The paper reported unpublished results of investigations on the catalytic addition of silanes containing silicon-attached hydrogen to unsaturated and aromatic compounds, on the high-temperature condensation of such silanes with alkyl, aryl, and alkenyl halides, and on the synthesis of butadienylsilanes, (trialkylsilyl)acrylic acids, (trialkylsilyl)styrenes, and silicon-containing vinyl ethers and acetals. It was shown that in some syntheses chloroplatinic acid has great advantages over platinum on carriers as a catalyst. Among the numerous new silicon-containing monomers synthesized by A. D. Petrov's group there are many which contain unsaturated bonds. These compounds are of special interest because of their ability to polymerize.

In the discussion on the paper, Corresponding Member of the Academy V. V. Korshak said "As a result of the work of A. D. Petrov's group much interesting material has been obtained which enables us to reach conclusions regarding the effect of silicon in various groups on the reactivities of these compounds, particularly in polymerization reactions.

Particularly great interest was taken in R. Kh. Freidlina's paper on "Homolytic Isomerization in Solutions," which showed that in the homolytic addition of HBr, Br_2, or CCl_3Br to suitable polyhaloalkenes ($CCl_3CX=CH_2$, in which X = H, Cl, Br, CH_3, and $CHCl_2CH=CH_2$) in presence of benzoyl peroxide, homolytic rearrangement of radicals occurs. A free-radical chain mechanism was proposed for these reactions. A homolytic molecular rearrangement was discovered and was studied for the case of 2-bromo-3,3,3-trichloropropene; a chain mechanism was proposed. The telomerization of ethylene with tetrachloroethylene was investigated; this gives tetrachloroalkenes containing even numbers of carbon atoms in their molecules.

R. Kh. Freidlina's paper prompted a very lively exchange of views; the participants in the discussion included Academicians I. L. Knuniants, A. D. Kursanov, A. N. Nesmeianov, and N. N. Semenov, Corresponding Members of the Academy V. V. Nekrasov, Ia. K. Syrkin, and A. D. Petrov, and others.

I. L. Knuniants stated that R. Kh. Freidlina's work on homolytic isomerization in solutions was an event of great importance in organic chemistry.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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